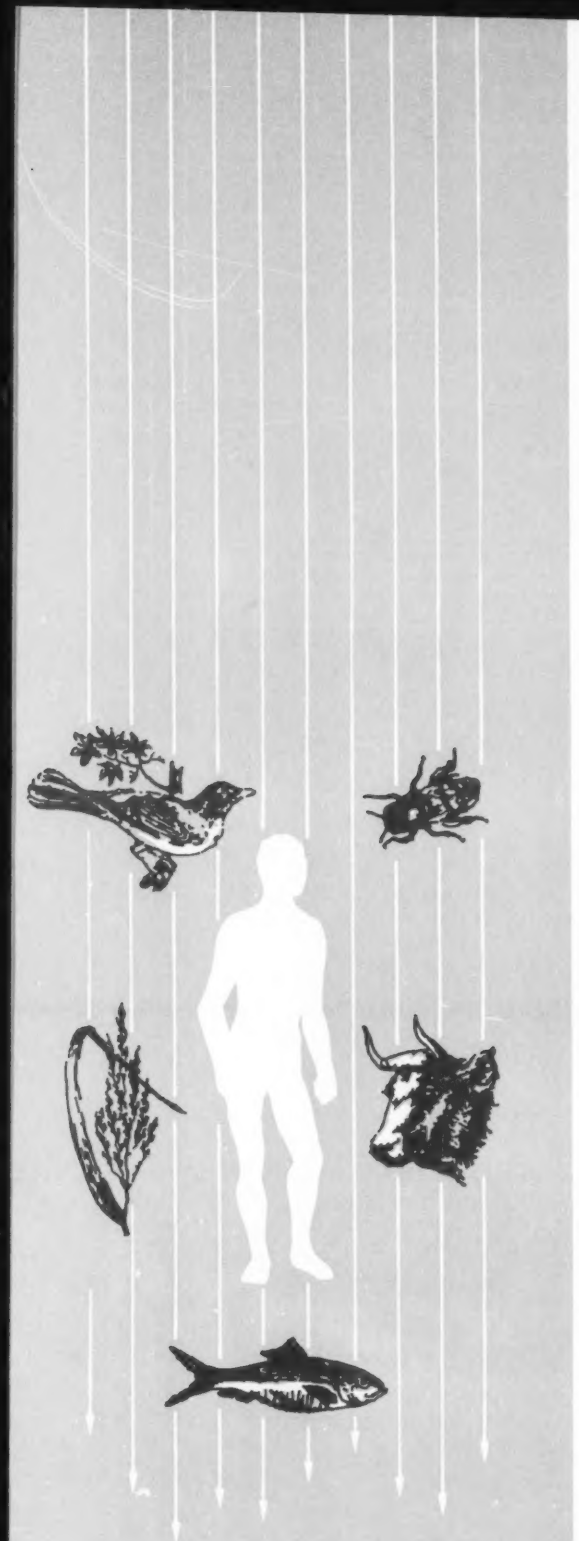

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The Working Group is comprised of representatives of the U.S. Departments of Agriculture; Commerce; Defense; the Interior; Health, Education, and Welfare; State; Transportation; and Labor; and the Environmental Protection Agency.

The Monitoring Panel consists of representatives of the Agricultural Research Service, Animal and Plant Health Inspection Service, Extension Service, Forest Service, Department of Defense, Fish and Wildlife Service, Geological Survey, Food and Drug Administration, Environmental Protection Agency, National Marine Fisheries Service, National Science Foundation, and Tennessee Valley Authority.

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Pesticide monitoring activities of the Federal Government, particularly in those agencies represented on the Monitoring Panel which participate in operation of the national pesticides monitoring network, are expected to be the principal sources of data and articles. However, pertinent data in summarized form, together with discussions, are invited from both Federal and non-Federal sources, including those associated with State and community monitoring programs, universities, hospitals, and nongovernmental research institutions, both domestic and foreign. Results of studies in which monitoring data play a major or minor role or serve as support for research investigation also are welcome; however, the Journal is not intended as a primary medium for the publication of basic research. Publication of scientific data, general information, trade names, and commercial sources in the *Pesticides Monitoring Journal* does not represent endorsement by any Federal agency.

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FISH, WILDLIFE, AND ESTUARIES

Polychlorinated Biphenyls and Other Organic Chemical Residues in Fish from Major Watersheds of the United States, 1976

Gilman D. Veith, Douglas W. Kuehl, Edward N. Leonard, Frank A. Puglisi, and Armond E. Lemke [1]

ABSTRACT

Composite samples of fish were collected from major United States watersheds in 1976 and analyzed for PCBs and related organic chemicals. PCBs were found in 93 percent of the fish samples; 53 percent of the samples contained more than 5 ppm PCBs, whole fish basis, which is the current tolerance level set by the Food and Drug Administration, U.S. Department of Health, Education and Welfare. Only 14 percent of the samples contained less than the proposed action level of 2 ppm PCBs. PCB concentrations ranged from less than 0.3 ppm to 140 ppm in the composite samples. ΣDDT concentrations ranged from less than 0.05 ppm to 4.53 ppm. Hexachlorobenzene was identified in 19 percent of the samples, and chlordane components were identified in 36 percent of the samples. Chemicals identified by gas chromatography/mass spectrometry but not quantified include chlorinated benzenes, styrenes, anisoles, phenols, anilines, propanes, and butadienes, as well as mixtures of petroleum hydrocarbons.

Introduction

The intent of this study was to identify by gas chromatography/mass spectrometry (GC/MS) major PCB components in fish from as many watersheds as possible. Particular attention was given to the occurrence of the lesser chlorinated PCBs having 2, 3, and 4 chlorine atoms. In response to the September-November 1976 litigation on the proposed toxic pollutant effluent standards for PCBs, requests for the collection of composite fish samples from major United States watersheds were sent to each regional office of the U.S. Environmental Protection Agency in spring 1976 (*6*).

Each region was initially requested to send 10-lb composite samples of fish from the lower reaches of waters that, in the opinion of the regional staff, were major drainages. Such samples are not adequate for monitoring programs aimed at establishing relative concentrations of residues or trends in residues from year to year. However, residue-forming chemicals accumulate in any aquatic organism even though the extent of accumulation may vary with the species. Consequently, primary emphasis was placed on the identification of accumulating chemicals; the quantities of these chemicals were of secondary importance.

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Methods and Procedures

PREPARATION OF SAMPLES

Fish samples were collected by state and federal field crews and shipped frozen to the Environmental Research Laboratory, Duluth, Minnesota. Fish samples were homogenized as a composite and given laboratory numbers consecutively from 1 to 58. Subsamples weighing 20 g and 30 g were exhaustively extracted on a Soxhlet extractor with a 1:1 mixture of hexane and methylene chloride. In addition, 10 samples showing comparatively large quantities or numbers of chemicals were selected for more detailed GC/MS analyses in which the extract of a 100-g subsample was used.

The 20-g sample extract was concentrated and placed on a 20-g Florisil column. PCBs and related chemicals were eluted with 250 ml hexane, and the extract was concentrated to 100 ml for initial electron-capture analysis. Recovery of PCBs and DDE from spiked samples was 85 ± 4 percent, and has been presented in detail previously (*7*).

The 30-g and 100-g samples were concentrated on a Kuderna-Danish concentrator and a 3-ball Snyder column to a lipid concentration of 100 μg/ml in methylene chloride for cleanup by gel permeation chromatography (*5*). The extract was cleaned by sequential elution of 5-ml aliquots on a 60-cm × 2-cm bed of SX-2 Bio-Beads (Bio-Rad Laboratories); methylene chloride was used as a solvent. The combined 160–225-ml fraction containing the PCBs from each extract was passed through a

column containing 15 g Celite 545 impregnated with 9 ml of a 1:1 mixture of H_2SO_4 and fuming H_2SO_4 (30 percent SO_3). The extract was concentrated to 1–3 ml for screening on a flame ionization detector before GC/MS analysis. Recoveries of PCBs and related nonpolar chemicals are greater than 90 percent by this procedure (*5*).

ELECTRON-CAPTURE ANALYSIS

Analyses of 20-g sample extracts for PCBs were performed on a Hewlett-Packard Model 5700A gas chromatograph equipped with a Model 3352B Laboratory Data System, an automatic sampler, and linearized argon-methane detector. Instrument parameters and operating conditions follow:

Column:	glass, 6 ft × ⅛ inch ID, packed with 80–100-mesh Gas-Chrom Q coated with a mixture of 4 percent SE-30 and 6 percent OV-210.
Column temperature:	programmed from 160° to 220°C at 2°/minute, followed by an 8-minute hold at 220°C.
Carrier gas:	a mixture of 90 percent argon and 10 percent methane flowing at 30 ml/minute.

The chromatograms were interpreted by a computer program in which 16 reference PCB peaks were monitored. Eight reference peaks corresponded to PCBs found in Aroclor 1016 (or Aroclor 1242), and eight reference peaks corresponded to PCBs found in Aroclor 1254. The program estimated the quantity of the Aroclor 1016/1242 or Aroclor 1254 by comparing them with the individual peak areas obtained for standard Aroclor mixtures. The means and standard deviations of the respective mixtures, based on all reference peaks found, were computed, and peaks with areas more than twice the standard deviation were considered to be contaminated by an interfering chemical and were eliminated from the PCB estimate of the mixture. At least four of the eight reference peaks were required to be present before a PCB mixture could be identified.

GC/MS ANALYSIS

Extracts of the 30-g and 100-g tissue samples were screened by using a flame ionization detector (FID) and then were subjected to analysis by GC/MS.

The GC/MS analyses for both 30-g and 100-g samples were performed on a Varian Mat Ch-5 mass spectrometer interfaced with a Varian Model 620i modified data system (*2*). Instrument parameters and operating conditions were as follows:

Column:	glass, 6 ft × ⅛ inch ID, packed with 80–100-mesh Gas-Chrom Q coated with 3 percent OV-101
Column temperature:	programmed from 100° to 225°C at 4°/minute, followed by a 5-minute hold at 100°C.

Spectra were acquired repetitively every 7 seconds at 3.5 seconds/mass decade. Resolution was 1000 during the gas chromatographic elution period. After mass conversion on the 620i computer, spectra were transmitted to Varian Model 620L computer for data formatting and analysis. The GC/MS data were screened by selecting ions in the mass spectra of chemicals of interest and searching all of the spectra for the GC peaks where the ions occurred most intensely (*4*).

Results and Discussion

A summary of sampling areas, sample composition, and estimates of PCB concentrations are given in Table 1. Of the 58 samples analyzed, 93 percent contained measurable quantities of PCBs. The total PCB concentrations, whole fish basis, ranged from less than 0.3 ppm to a maximum of 140 ppm in the composite sample from Lake Hartwell, South Carolina (Region IV). Approximately 86 percent of the samples contained more than 2 ppm PCBs, 53 percent contained more than 5 ppm PCBs, and 21 percent contained more than 10 ppm PCBs. The high concentrations of PCBs in fish from the Acushnet, Hoosic, and Merrimack Rivers in Massachusetts, Choccolocco Creek in Alabama, Coosa and Altamaha Rivers in Georgia, Lake Hartwell in South Carolina, Fort Loudoun Reservoir in Tennessee, Saginaw River in Michigan, Lake Michigan in Wisconsin, and the Huron River in Ohio suggest that these watersheds are receiving comparatively high concentrations of PCBs.

Composition of the PCB mixtures in fish residues is especially noteworthy because of the frequency of PCB components resembling Aroclor 1016 and Aroclor 1242 formulations. Although PCB components similar to those in Aroclor 1254 accounted for over 80 percent of the total PCB residue in the majority of the samples (Table 1), PCB residues similar to Aroclors 1016 and 1242 were found in 71 percent of the samples. Moreover, Aroclor 1016 and 1242 residues were equal to or greater than the Aroclor 1254 residues in 16 percent of the samples. The highest Aroclor 1016 and 1242 residues were found in the Acushnet River and Lake Hartwell where concentrations were 25.2 ppm and 42.5 ppm, respectively. These data refute contentions that Aroclors 1016 and 1242 do not persist in the environment.

Hexachlorobenzene (HCB) was confirmed by GC/MS in 19 percent of the watershed samples (Table 2). Even though acceptable spectra which unequivocally identify HCB could not be obtained for more than 19 percent of the samples, the electron-capture gas chromatograms suggested that HCB was present at comparatively low concentration in an additional 33 percent of the samples. HCB concentrations ranged from less than 0.005 ppm in 48 percent of the samples to a maximum of 11.6 ppm in a composite sample of eels from the Altamaha River at Darien, Georgia. Approximately 15 percent of the 58 samples contained more than 0.1 ppm HCB. The rivers that were most contaminated with HCB were the

TABLE 1. *Concentration of PCBs in 58 composite whole fish samples from major United States watersheds, 1976*

Sampling Area	Sample Composition	Lab. Ident.	PCB Residues, ppm 1016-1242	1254	Total
EPA—REGION I					
Kennebec River, southwest area of Merry Meeting Bay, Sagadahoc County, Me.	6 white sucker 3 white perch	76072	2.55	4.90	7.45
Connecticut River, ¼ mile north of Vernon Dam near Hinsdale, N.H.	9 white sucker	76079	0.56	2.10	2.66
Penobscot River near East Eddington, Me.	10 white sucker	76112	0.19	5.80	5.99
Acushnet River Reservoir near New Bedford, Mass.	32 sea perch	76116	25.2	22.0	47.2
Hoosic River near North Adams, Mass.	5 longnose sucker 20 white sucker	76118	7.45	4.74	12.2
Merrimack River, ½ mile upstream from Lowell, Mass.	2 sucker 30 sucker 2 catfish 1 carp 1 goldfish 3 bass	76121	0.58	11.1	11.68
EPA—REGION IV					
Choccolocco Creek, 1 mile above Highway 71 bridge in Talladega County near Anniston, Ala.	2 goldfish 4 channel catfish 4 gizzard shad 1 redear sunfish 4 largemouth bass	76064	10.5	78.8	89.3
Coosa River above Weiss Reservoir, Cherokee County, Ga., and Alabama state line	2 goldfish 1 carp 4 largemouth bass 4 gizzard shad 2 bullhead catfish	76065	5.00	60.0	65.0
Savannah River, Ga.	1 black crappie 5 channel catfish 1 bullhead catfish 2 redhorse sucker 1 summer flounder 1 largemouth bass 1 white catfish 1 striped bass	76066	<0.10	3.07	3.07
Lake Hartwell, S.C.	3 carp sucker 3 white catfish 1 channel catfish 1 carp	76068	42.5	97.5	140
Coosa River at Rome, Ga.	2 channel catfish 1 largemouth bass 1 black crappie 1 white bass 1 gizzard shad 1 smallmouth buffalo 1 spotted sucker 1 carp	76069	5.29	69.7	75.0
Duck River below Columbia, Murfreesboro, Tenn.	2 channel catfish 6 carp sucker 2 redhorse sucker	76070	5.29	3.78	9.07
Dennison Slough at Wilson Reservoir, Ala.	3 gar 6 gizzard shad 3 largemouth bass 3 redear sunfish	76071	0.26	74.00	77.26
Chattahoochee River, Albany, Ga.	3 largemouth bass 1 black crappie 1 white catfish	76073	2.54	4.92	7.46
Lake Jackson, Ga., immediately above dam	8 largemouth bass 5 bluegill 2 redbreast sunfish 8 bullhead 1 warmouth	76074	<0.10	<0.20	<0.3
Altamaha River, Darien, Ga.	7 American eel	76075	<0.10	24.5	24.5
Chattahoochee River below W. F. George Reservoir at Albany, Ga.	1 carp 1 largemouth bass 1 black crappie 1 white catfish 1 bluegill	76082	4.15	4.28	8.43
Chattahoochee River at Route 166 bridge, Atlanta, Ga.	6 carp 1 spotted bass	76083	5.29	3.78	9.07
Nickajack Tailwater from the Tennessee Wildlife Resource Agency at Cookeville, Tenn.	4 catfish	76089	0.76	5.87	6.63
St. John's River at Cross Creek, Crescent City, Fla.	4 channel catfish	76090	<0.10	2.62	2.62
Cumberland River at Navigation Mile 93.5 Barkley Reservoir in Nashville, Tenn.	1 blue catfish 2 carp 2 channel catfish 2 drum	76105	0.16	3.20	3.36
Duck River mouth at Tennessee Navigation Mile 111, Tenn.	1 blue catfish 2 carp	76106	0.11	1.04	1.15

(Continued next page)

TABLE 1 (cont'd.). *Concentration of PCBs in 58 composite whole fish samples from major United States watersheds, 1976*

Sampling Area	Sample Composition	Lab. Ident.	PCB Residues, ppm 1016-1242	1254	Total
EPA—REGION IV (cont'd)					
Pee Dee River, 15 miles above Georgetown, S.C.	7 bullhead 1 perch 2 sunfish	76111	0.12	0.56	0.68
Fort Loudoun Reservoir between Alcoa Highway bridge and Knoxville's Third Creek Sewage Treatment Plant, Morristown, Tenn.	2 catfish 1 smallmouth buffalo	76113	2.48	22.2	24.7
Roanoke River, Raleigh, N.C.	8 white catfish 1 brown bullhead 1 channel catfish	76124	0.22	2.70	2.92
Cape Fear River upstream from Black River at confluence of Hood Creek, N.C.	3 yellow bullhead 2 white catfish 2 brown bullhead 1 channel catfish 1 carp	76127	<0.10	1.99	1.99
EPA—REGION V					
Grand River, Station No. 3, Mich.	3 channel catfish 1 redhorse	76067	<0.10	0.75	0.75
Wabash River, Station No. 1, Evansville, Ind.	3 drum	76076	<0.10	7.88	7.88
Saginaw River below Tittabawassee River, Mich.	1 perch 1 drum 1 sucker	76077	6.08	5.85	11.9
Ohio River, Gallipolis, Oh.	9 channel catfish	76078	1.04	1.87	2.91
St. Joseph River, Station No. 3, Mich.	1 dogfish 1 sucker 3 catfish 1 rock bass	76081	0.94	4.40	5.34
Saginaw River mouth above power plant, Mich.	13 catfish 1 drum	76085	4.90	3.65	8.55
Saginaw River below Cheyboyganing Creek, Mich.	3 perch 1 catfish 1 drum	76086	3.24	5.68	8.92
Detroit River off end of Grosse Ile, Mich.	2 carp	76087	2.38	4.90	7.28
Grand River, Station No. 2, Mich.	3 sucker 2 rock bass	76093	0.44	1.83	2.27
Rocky River mouth, Oh.	1 carp 3 bullhead 5 drum 1 goldfish	76095	<0.10	3.44	3.44
Wabash River, Station No. 2, Evansville, Ind.	1 bowtin	76096	<0.10	5.90	5.90
Wabash River, Station No. 3, Evansville, Ind.	6 catfish 9 drum	76097	1.01	2.20	3.21
Green Bay area south of Long Tail Point, Wis.	5 carp	76123	13.1	6.3	19.4
Illinois River, Peoria Lake, Ill.	3 drum 3 carp	76125	2.66	4.34	7.00
St. Louis River, Mich.	1 walleye 1 northern	76103	<0.10	2.25	2.25
St. Joseph River, Station No. 1, Mich.	4 bullhead 1 rock bass	76109	0.18	3.86	4.04
Maumee River, Oh.	2 carp 1 catfish	76110	0.31	5.05	5.36
Huron River mouth, Oh.	3 goldfish 2 carp 1 bullhead 2 channel catfish 4 white bass 6 drum	76119	9.22	2.65	11.9
Ashtabula River, Oh.	3 alewives 9 gizzard shad 3 white bass 1 yellow perch 3 bullhead	76120	4.46	2.74	7.2
Red River, North Halstad, Minn.	6 carp 1 channel catfish 1 redhorse 1 goldeye	76122	0.28	3.55	3.83
Morgan's Point in Houston ship channel, Tex.	24 gizzard shad 12 sabre fish 30 croaker 4 cutlassfish	76080	0.14	1.98	2.12
Lower White River, Ark.	5 freshwater drum 1 carp 1 catfish	76084	<0.10	<0.20	<0.3
Arkansas River, Site 22B, Ark.	2 channel catfish 1 freshwater drum	76088	<0.10	<0.20	<0.3
Lower Arkansas River, Ark.	3 catfish 2 freshwater drum	76094	0.28	2.60	2.88
Arkansas River, Site 22A, Ark.	4 carp	76104	<0.10	<0.20	<0.3

(Continued next page)

TABLE 1 (cont'd.). *Concentration of PCBs in 58 composite whole fish samples from major United States watersheds, 1976*

Sampling Area	Sample Composition	Lab. Ident.	PCB Residues, ppm		
			1016-1242	1254	Total
EPA—REGION V (cont'd)					
Coody Creek mouth, Muskogee, Okla.	2 carp 2 smallmouth buffalo 1 bigmouth buffalo	76107	<0.10	6.94	6.94
Nueces Bay, Corpus Christi, Tex.	1 alligator gar 1 striped mullet 1 gulf menhaden 3 spotted seatrout	76108	0.11	3.19	3.30
Adams Bayou at F.M. 1006 in Orange, Tex.	1 alligator gar 1 European carp	76114	<0.10	2.99	2.99
Adams Bayou at F.M. 1006 in Orange, Tex.	1 alligator gar 1 European carp	76115	<0.10	5.30	5.30
FISH AND WILDLIFE SERVICE ALBUQUERQUE, N.M.					
Morgan Lake, N.M.	5 carp 5 channel catfish 2 bluegill 1 green sunfish	76092	<0.10	4.47	4.47
Colorado River, Blythe, Calif.	3 channel catfish 1 bluegill 4 treadfin shad	76126	0.22	3.33	3.55
Rio Grande River, Elephant Butte, N.M.	1 bluegill 1 crappie 1 walleye 3 white bass 1 softshell turtle 1 carp sucker 2 buffalo 1 carp 1 catfish 1 black bullhead 1 channel catfish 2 northern 1 shad 1 largemouth	76117	0.15	3.94	4.09

Altamaha River; the Wabash River, Evansville, Indiana; the Ashtabula River, Ohio; and the Saginaw River, Michigan.

ΣDDT concentrations in fish collected in this study were much smaller than expected (Table 2). DDT concentration was below the determinable limit of 0.05 ppm in approximately 9 percent of the samples, and 59 percent of the samples contained less than 1 ppm ΣDDT. The maximum DDT concentration of 4.53 ppm was found in composite samples from the Coosa River, Georgia. Residues of DDT probably have decreased significantly since its use was banned from the United States in 1972. In contrast to earlier work where DDT was a predominant contaminant in fish in many watersheds, measuring DDT residues is now a much greater analytical problem because of their small concentrations compared to other chemical contaminants.

Chlordane and nonachlor isomers were identified in 36 percent of the samples (Table 2). Residues could not be quantified, however, because of inadequate separation of these chemicals from interferences in the samples.

Ten samples gave atypical chromatograms and were subjected to more detailed GC/MS analyses to identify the major chemical residues. Table 3 presents a summary of the chemicals found in these samples. Authors followed specific techniques developed for measuring chemical residues found most commonly in fish from the Great Lakes. The list of chemicals in Table 3 excludes the numerous PCB homologs and the hydrocarbons which were identified. The Saginaw, Detroit, Ohio, Arkansas, and Ashtabula Rivers contained numerous chlorinated benzenes. The chlorinated styrenes and, in particular, octachlorostyrene previously reported by Kuehl et al. (*3*), were present in the Saginaw, Detroit, and Ashtabula Rivers. These residues are of interest because the authors have been unable to identify any industry in the United States which produces these chemicals. In the present study, the Ashtabula River contained the greatest variety of organochlorines in addition to a series of polychlorinated butadienes, chlorinated propane and propene, and chlorinated norbornenes.

Although only semiquantitative, the amounts of the chemicals in a sample relative to the other samples from this study and other ongoing research can be estimated from the ion intensities in the reconstructed mass chromatograms used in the GC/MS analyses. From

TABLE 2. *Concentrations of ΣDDT and HCB and occurrence of chlordane and nonachlor in 58 composite whole fish samples from major United States watersheds, 1976*

Sampling Area	Lab. Ident.	ΣDDT, ppm	HCB (C_6Cl_6), ppb	Chlordane		Nonachlor	
				cis	trans	cis	trans
EPA—REGION I							
Kennebec River in the southwest area of Merry Meeting Bay, Sagadahoc County, Me.	76072	0.59	20	—	—	—	—
Connecticut River, ¼ mile north of Vernon Dam near Hinsdale, N.H.	76079	<0.05	<5	—	—	—	—
Penobscot River near East Eddington, Me.	76112	0.11	<5	—	—	—	—
Acushnet River Reservoir near New Bedford, Me.	76116	1.68	<5	—	—	—	—
Hoosic River near North Adams, Mass.	76118	1.95	81	—	—	—	—
Merrimack River, ½ mile upstream from Lowell, Mass.	76121	0.33	39	X*	X*	X	X
EPA—REGION IV							
Choccolocco Creek 1 mile above Highway 71 bridge in Talladega County near Anniston, Ala.	76064	<0.05	<5	—	—	—	—
Coosa River above Weiss Reservoir, Cherokee County, Ga. and Alabama state line	76065	4.53	<5	—	—	—	—
Savannah River, Ga.	76066	0.21	<5	—	—	—	—
Lake Hartwell, S.C.	76068	<0.05	<5	—	—	—	—
Coosa River at Rome, Ga.	76069	4.06	<5	—	—	—	—
Duck River below Columbia, Murfreesboro, Tenn.	76070	0.71	<5	—	—	—	—
Dennison Slough at Wilson Reservoir, Ala.	76071	3.60	5	—	—	—	—
Chattahoochee River, Albany, Ga.	76073	2.52	<5	X	X	X	X
Lake Jackson, Ga., immediately above dam	76074	0.91	7	X	X	X	X
Altamaha River, Darien, Ga.	76075		11,600	—	—	—	—
Chattahoochee River below W. F. George Reservoir at Albany, Ga.	76082	1.24	<5	X	X	X	X
Chattahoochee River at Route 166 bridge, Atlanta, Ga.	76083	<0.05	<5	X	X	X	X
Nickajack Tailwater from the Tennessee Wildlife Resource Agency at Cookeville, Tenn.	76089	3.20	53	X	X	X	X
St. John's River at Cross Creek, Crescent City, Fla.	76090	0.62	<5	—	—	—	—
Cumberland River at Navigation Mile 93.5 Barkley Reservoir, Nashville, Tenn.	76105	0.62	6	—	—	—	—
Duck River mouth at Tennessee Navigation Mile 111, Tenn.	76106	0.34	<5	—	—	—	—
Pee Dee River 15 miles above Georgetown, S.C.	76111	0.09	128	—	—	—	—
Fort Loudoun Reservoir between Alcoa Highway bridge and Knoxville's Third Creek Sewage Treatment Plant, Morristown, Tenn.	76113	3.86	70	X	X	—	X
Roanoke River, Raleigh, N.C.	76124	1.16	<5	—	—	—	—
Cape Fear River upstream from Black River at confluence of Hood Creek, N.C.	76127	0.16	45	—	—	—	—
EPA—REGION V							
Grand River, Station No. 3, Mich.	76067	2.26	19	X	X	X	X
Wabash River, Station No. 1, Evansville, Ind.	76076	1.66	1,310	X	X	X	X
Saginaw River below Tittabawassee River, Mich.	76077	1.88	490	—	—	—	—
Ohio River, Gallipolis, Oh.	76078	0.28	137	X	X	X	X
St. Joseph River, Station No. 3, Mich.	76081	4.05	16	X	X	X	X
Saginaw River mouth above power plant, Mich.	76085	0.23	131	—	—	—	—
Saginaw River below Cheyboyganing Creek, Mich.	76086	1.08	237	—	—	—	—
Detroit River off end of Grosse Ile, Mich.	76087	1.14	167	—	—	—	—
Grand River, Station No. 2, Mich.	76093	1.93	<5	X	X	X	X
Rocky River mouth, Oh.	76095	0.28	14	X	X	X	X
Wabash River, Station No. 2, Evansville, Ind.	76096	0.27	21	X	X	X	X
Wabash River, Station No. 3, Evansville, Ind.	76097	0.26	34	X	X	X	X
Green Bay area south of Long Tail Point, Wis.	76123	1.14	14	—	—	—	—
Illinois River, Peoria Lake, Ill.	76125	0.65	<5	X	X	X	X
St. Louis River, Minn.	76103	0.12	5	—	—	—	—
St. Joseph River, Station No. 1, Mich.	76109	0.45	<5	—	—	—	—
Maumee River, Oh.	76110	0.13	<5	—	—	—	—
Huron River mouth, Oh.	76119	0.61	74	X	X	X	X
Ashtabula River, Oh.	76120	0.13	3,140	—	—	—	—
Red River, North Halstad, Minn.	76122	0.19	<5	—	—	—	—
EPA—REGION VI							
Morgan's Point in Houston ship channel, Tex.	76080	0.05	53	—	—	—	—
Lower White River, Ark.	76084	2.83	68	—	—	—	—
Arkansas River, Site 22B, Ark.	76088	1.03	<5	—	—	—	—
Lower Arkansas River, Ark.	76094	3.59	<5	—	—	—	—
Arkansas River, Site 22A, Ark.	76104	1.22	7	X	X	X	X
Coody Creek mouth, Muskogee, Okla.	76107	1.08	<5	X	X	X	X
Nueces Bay, Corpus Christi, Tex.	76108	0.33	83	X	X	X	X
Adams Bayou at F.M. 1006, Orange, Tex.	76114	0.31	<5	—	—	—	—
Adams Bayou at F.M. 1006, Orange, Tex.	76115	0.44	<5	X	X	X	X
FISH AND WILDLIFE SERVICE ALBUQUERQUE, N.M.							
Morgan Lake, N.M.	76092	<0.05	<5	—	—	—	—
Colorado River, Blythe, Calif.	76126	0.37	<5	—	—	—	—
Rio Grande River, Elephant Butte, N.M.	76117	0.11	<5	—	—	—	—

NOTE: X = positive; — = negative; * = GC/MS confirmation of this chemical in sample.

TABLE 3. *Organochlorines except PCBs identified by GC/MS analysis of selected composite whole fish samples from major United States watersheds, 1976*

Compounds Identified	Saginaw R. 77104	Detroit R. 77103	Ark. R. 77102	Ohio R. 77101	Ashtabula R. 77098	Wabash R. 77099	Lower White R. Ark. 77159	Morgans Pt. 77139	Ill. R. 77106	Green Bay Lake Mich.
Dichlorobenzene I*	X			X						X
Dichlorobenzene II	X									
Trichlorobenzene I	X		X							
Trichlorobenzene II	X									
Tetrachlorobenzene I	X		X		X					
Tetrachlorobenzene II	X		X							
Pentachlorobenzene	X		X		X	X				
Hexachlorobenzene	X	X	X	X	X	X				
Hexachlorostyrene I					X					
Hexachlorostyrene II					X					
Heptachlorostyrene I	X				X					
Heptachlorostyrene II					X					
Octachlorostyrene	X	X			X					
Trichloroanisole			X							
Pentachloroanisole		X								
cis-Chlordane		X	X	X	X				X	X
trans-Chlordane				X					X	X
cis-Nonachlor									X	
trans-Nonachlor		X	X	X	X				X	X
Dichloronaphthalene			X							
DDE	X		X		X	X		X	X	
TDE			X			X				
DDT			X			X				
Pentachlorobenzyl alcohol						X				
Pentachlorophenol						X				
Tetrachlorobutadiene I					X					
Tetrachlorobutadiene II					X					
Pentachlorobutadiene I					X					
Pentachlorobutadiene II					X					
Hexachlorobutadiene					X	X				
Tetrachloropropene					X					
Pentachloropropane					X					
Pentachloronorbornene					X					
Heptachloronorbornene						X				
Heptachloronorbornadiene						X				
Chlordene isomer						X				
Heptachlor isomer						X				
Dihydroheptachloro isomer						X				
Heptachlor epoxide						X				
Hexachlorocyclopentane							X			

NOTE: Roman numerals indicate different isomers found. Other compounds tested for and not found were pentachloroaniline, pentachlorotoluene, mirex, photomirex, α-hexachlorocyclohexane, γ-hexachlorocyclohexane, oxychlordane, toxaphene ($C_{10}H_8Cl_7$), toxaphene ($C_{10}H_7Cl_8$), pentachlorohydroxy biphenyl, hexachlorohydroxy biphenyl, heptachlorohydroxy biphenyl, hexachlorostyrene III, heptachlorostyrene III, tetrachloroanthracene, and DDMU.

these analyses, the following determinations were made: Arkansas River fish contained high concentrations of trichloroanisole, which was not identified in any other watershed. Wabash River fish contained high concentrations of pentachlorophenol, pentachlorobenzyl alcohol, heptachloronorbornene, and hexachlorobornadiene. Detroit River fish contained high concentrations of pentachloroanisole. Lower White River fish contained high concentrations of hexachlorocyclopentane.

Large amounts of hydrocarbons were also present in many of the samples, and considerable effort was made to identify the components. With a few exceptions, however, the majority of the hydrocarbons exist as complex mixtures of unresolved peaks that cannot presently be explicitly characterized. Although the hydrocarbons are generally not observed in monitoring studies involving electron-capture gas chromatography, they are readily observed when a flame ionization detector is used.

The majority of the hydrocarbon mixtures consist of saturated and unsaturated hydrocarbons similar to those found in petroleum products. Although the mixtures vary greatly among the samples, there are apparently two major distributions of hydrocarbons of approximately 18 and 26 carbon atoms (Fig. 1).

Heptadecane, a 17-carbon straight-chain hydrocarbon, can be seen in many chromatograms as a peak eluting at approximately 18 minutes. Hydrocarbons with 18, 19, 20, or more carbons can be seen as peaks eluting at regular intervals in the chromatograms at retention times longer than heptadecane. Unfortunately, chromatograms of hydrocarbons appear more complex because of the peaks from the branched-chain and alkylaromatic hydrocarbons among the straight-chain, or normal, hydrocarbons in the mixture. Authors of the present study concluded that the clusters of hydrocarbons eluting near heptadecane are similar to those observed in fuel oil mixtures, and those eluting at higher temperatures are similar to heavier oils such as crankcase oil. Because heptadecane is present at concentrations greater than 50 ppm, authors further conclude that many of the fish analyzed in the present study contain concentrations of hydrocarbons many times greater than concentrations of other contaminants and, in some cases, in quantities sufficient to simply weight the total residue. For example, Figure 2 presents the FID chromatogram of the Connecticut River, New Hampshire, fish extract in which the late-eluting hydrocarbons predominate the chromatogram.

From this preliminary work, authors do not conclude that all hydrocarbons found in fish are derived from contamination of the watersheds by petroleum. Indeed, heptadecane is thought to occur naturally, originating in benthic algae. The same is likely true of higher-molecular-weight *n*-paraffins such as those observed in Figure 3. Despite the high concentrations of PCBs in the Coosa River sample, the PCBs do not contribute significantly to the FID chromatogram, and the chromatogram resembles those obtained from fish caught in open waters of the Gulf of Mexico (*1*). It is characterized by a large heptadecane component and a series of other paraffins. If these are indicative of natural residues of hydrocarbons, the large clusters of hydrocarbons in Figures 1 and 2 which completely obscure the natural paraffins suggest contamination of the watershed by petroleum.

The characterization of these mixtures remains a major research problem in the exploration of contaminants in fish.

Acknowledgments

We thank all personnel of the regional offices of the U. S. Environmental Protection Agency and the Fish and Wildlife Service, U. S. Department of the Interior, who helped coordinate the collection of fish analyzed in this study.

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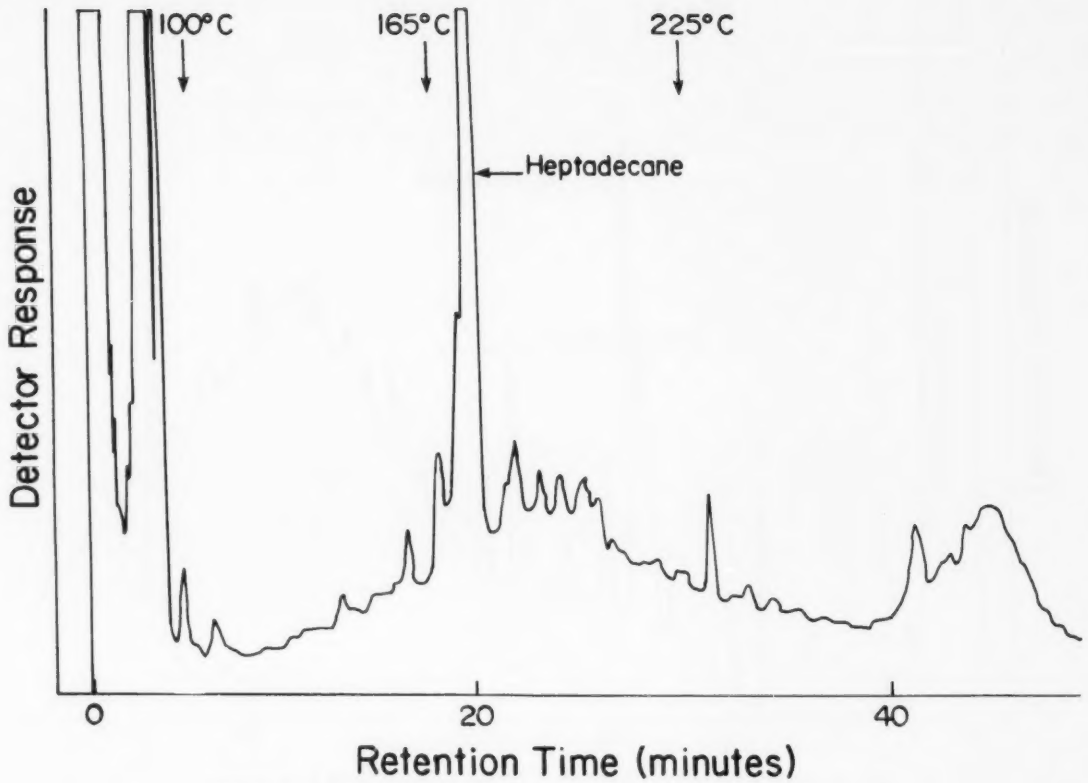

FIGURE 1. *Flame ionization detector chromatogram of whole fish extract from the Chattahoochee River, Georgia, 1976*

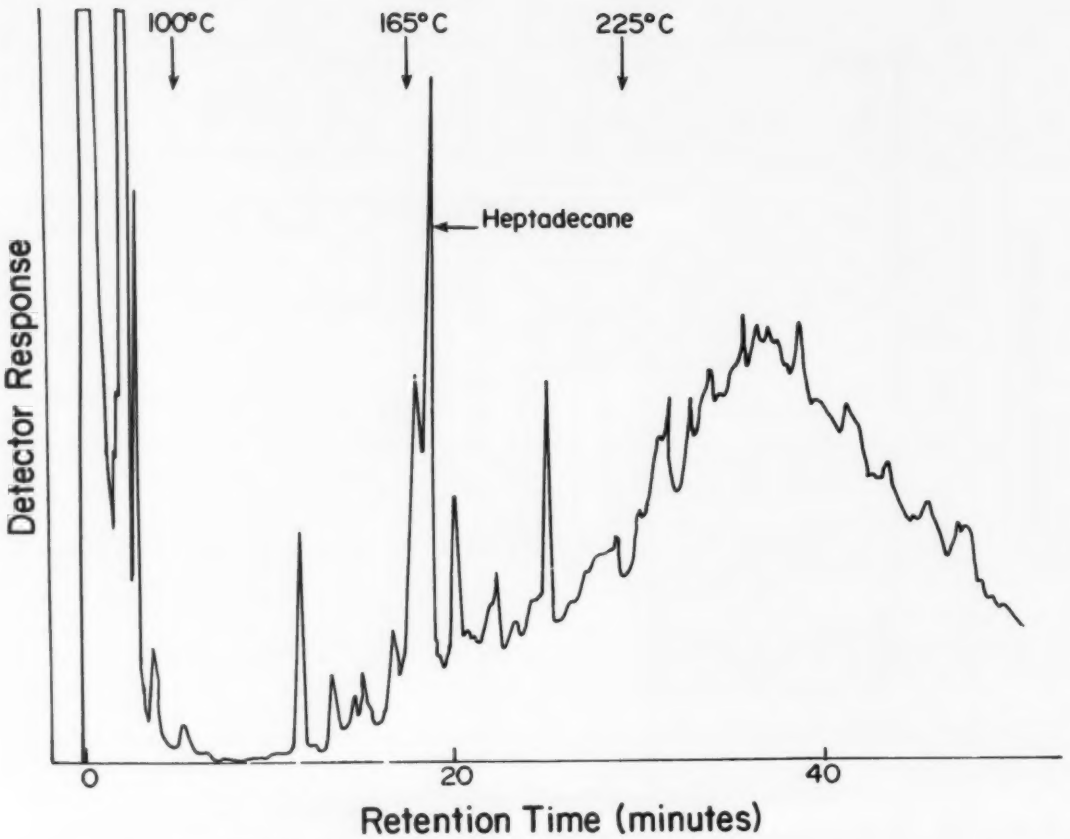

FIGURE 2. *Flame ionization detector chromatogram of whole fish extract from the Connecticut River, New Hampshire, 1976*

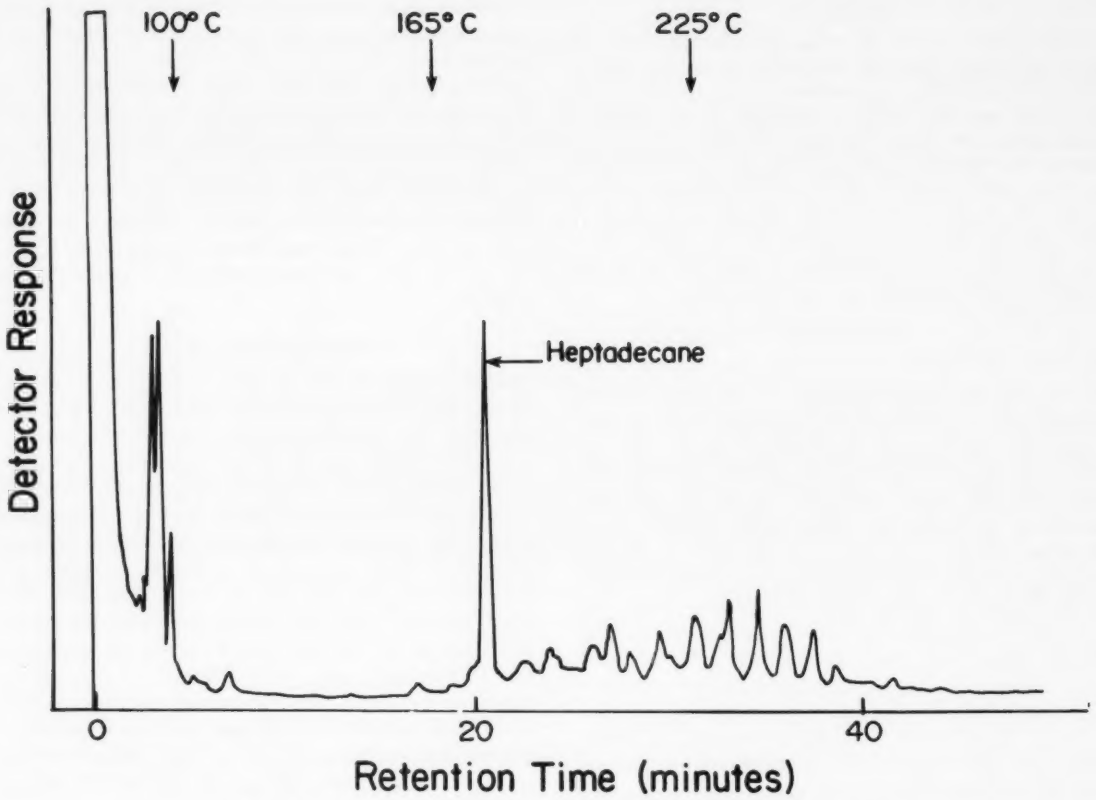

FIGURE 3. *Flame ionization detector chromatogram of whole fish extract from the Coosa River, Georgia, 1976*

Nationwide Residues of Organochlorine Compounds in Wings of Adult Mallards and Black Ducks, 1976–77

Donald H. White [1]

ABSTRACT

Organochlorine residues in wings of adult mallards and black ducks were monitored nationwide during the 1976–77 hunting season. DDE was found in all samples. Levels were unchanged since the 1972–73 collections in all migratory routes except the Pacific Flyway, in which residue levels declined significantly. Dieldrin levels had not changed in any flyway and residues remained low. PCB levels declined significantly in the Atlantic Flyway but remained stable in other flyways. Heptachlor epoxide, mirex, endrin, hexachlorobenzene, and chlordane isomers were detected in low amounts in some samples.

Introduction

The Fish and Wildlife Service, U.S. Department of the Interior, began nationwide monitoring of organochlorine pesticides in waterfowl wings during 1965–66 as part of the National Pesticide Monitoring Program. Samples were taken again in 1966–67 and subsequent collections were scheduled every third year to detect trends in residue levels. Wings of adult mallards (*Anas platyrhynchos*) and black ducks (*Anas rubripes*) are sampled because the combined ranges of these waterfowl cover the contiguous 48 states. Overall objectives and procedures have been discussed in earlier papers (*1–3*). The present paper gives the results of the 1976-77 duck wing collections, including mean residue levels for each state, a comparison of mean residues by major flyway for 1972–73 and 1976–77, and the percentage of pools containing each compound by major flyway. Major flyways are corridors comprised of states or parts of states through which large numbers of waterfowl migrate each spring and fall. The states that make up each of the four major flyways are listed in Table 1.

Collection Methods

Duck wings from the contiguous 48 states are available for monitoring purposes as a byproduct of a nationwide survey of waterfowl productivity. Cooperating hunters mailed wings of approximately 5,600 adult mallards and black ducks taken during the 1976–77 hunting season to a collection station within each flyway where wings were classified according to age and sex, and grouped according to state. Wings from each state were sorted systematically into pools of 25 wings. Pools from each state were selected randomly for chemical analysis; the number used was roughy proportional to each state's harvest. Pools were given a code number, placed in individually tagged plastic bags, and shipped in Dry Ice to Raltech Scientific Services, Inc., Madison, Wisconsin, for chemical analysis. Wings were stored frozen until analysis. A total of 227 pools were analyzed for organochlorine residues.

Analytical Procedures

Before being analyzed, the wings were plucked of most of the primary feathers and the distal joint (manus) was removed. The remaining portions were homogenized in a Hobart food grinder. A 40-g sample was weighed into a 250-ml beaker and mixed with 100 g anhydrous sodium sulfate. The sample was allowed to air dry overnight in a hood and was then transferred to a 43-mm × 123-mm prewashed Whatman extraction thimble plugged with glass wool. The thimble was placed in a desiccator overnight, and the sample was extracted on a Soxhlet extractor for 8 hours with a mixture of 150 ml ethyl ether and 150 ml petroleum ether. The extract was concentrated to near dryness on a steam bath and the remaining solvent was removed with nitrogen at room temperature. The residue was transferred to a 50-ml volumetric flask and diluted to volume with a 3:1 solution of toluene–ethyl acetate.

A 5-ml portion of the extract was placed on an Auto-Prep 1001 gel permeation chromatograph, standardized for organochlorine insecticides and PCBs. Instrument parameters and operating conditions follow:

Packing:	80 g of Bio-Beads (SX–3), 200–400-mesh
Column:	600 mm × 25 mm ID
Solvent:	3:1 toluene–ethyl acetate solution
Flow rate:	5.5 ml/minute
Dump time:	30 minutes
Collect time:	14 minutes
Wash time:	4 minutes

The resulting solution was concentrated on a flash

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evaporator to approximately 5 ml in the presence of 5 ml isooctane and was diluted to 25 ml with petroleum ether.

A 10-ml portion of the extract from the gel permeation chromatograph was placed on a 15-g standardized Silicar CC-4 column which had been washed to remove interfering compounds. Typical elutions follow:

Fraction I:	60 ml petroleum ether, contains HCB and mirex
Fraction II:	350 ml petroleum ether, contains PCBs and some DDE
Fraction III:	150-ml mixture of 1 percent acetonitrile, 19 percent hexane, and 80 percent methylene chloride, contains the remaining organochlorine compounds

Fractions I and II were concentrated on a steam bath to 1–2 ml and diluted to 10 ml with petroleum ether. Fraction III was concentrated on a flash evaporator to 1–2 ml and diluted to 10 ml with petroleum ether. Aliquots of 4 μl of each solution were injected into a gas chromatograph equipped with an electron-capture detector.

Analyses were performed on a Hewlett-Packard Model 5710A gas chromatograph equipped with a linear Ni^{63} detector and automatic injector, attached to a Hewlett-Packard Model 3352C data acquisition system. Instrument parameters and operating conditions for determining organochlorine pesticides and PCBs were:

Column:	1219 mm × 4 mm ID, glass, packed with a mixture of 1.95 percent OV–17 and 1.5 percent QF–1 on 80–100-mesh Supelcoport	
Temperatures, °C:	column	200
	injector	250
	detector	300
Carrier gas:	a mixture of 95 percent argon and 5 percent methane flowing at 33 ml/minute	

Instrument parameters and operating conditions for determining chlordane isomers were:

Column:	1219 mm × 4 mm ID, glass, packed with 3 percent OV–1 on 80–100-mesh Gas-Chrom Q	
Temperatures, °C:	column	190
	injector	250
	detector	300
Carrier gas:	a mixture of 95 percent argon and 5 percent methane flowing at 32 ml/minute	

TABLE 1. *Organochlorine residues in pools of wings of adult mallards and black ducks, 1976–77*

State	No. of Pools	Residues, ppm Wet Weight									
		DDE		DDT		TDE		Dieldrin		PCBs [1]	
		$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range
BLACK DUCKS, ATLANTIC FLYWAY											
Maine	4[2]	0.35±0.14 (4)	0.20–0.77	0.09±0.00 (1)	ND–0.09	0.03±0.01 (2)	ND–0.04	0.01±0.00 (3)	ND–0.02	0.38±0.05 (4)	0.29–0.49
Vermont	1[3]	0.15±0.00 (1)	—	ND	—	ND	—	ND	—	0.12±0.00 (1)	—
New Hampshire	1[2]	0.55±0.00 (1)	—	0.06±0.00 (1)	—	ND	—	0.01±0.00 (1)	—	0.64±0.00 (1)	—
Massachusetts	4[2]	0.39±0.13 (4)	0.04–0.67	0.08±0.02 (4)	0.06–0.14	0.02±0.01 (4)	0.01–0.04	0.08±0.05 (4)	0.02–0.22	0.96±0.13 (4)	0.70–1.31
Connecticut	2	0.36±0.00 (2)	0.35–0.36	0.05±0.01 (2)	0.03–0.06	0.02±0.00 (2)	0.01–0.02	0.03±0.00 (2)	—	1.11±0.28 (2)	0.83–1.38
Rhode Island	1	0.12±0.00 (1)	—	0.11±0.00 (1)	—	0.03±0.00 (1)	—	0.15±0.00 (1)	—	0.49±0.00 (1)	—
New York	4	0.48±0.08 (4)	0.32–0.69	0.06±0.04 (3)	ND–0.13	0.02±0.00 (4)	0.01–0.03	0.03±0.00 (4)	0.02–0.04	0.81±0.23 (4)	0.45–1.48
Pennsylvania	2[2]	0.25±0.09 (2)	0.16–0.34	0.02±0.00 (1)	ND–0.02	0.01±0.00 (1)	ND–0.01	ND	—	0.38±0.02 (2)	0.35–0.40
New Jersey	5	0.45±0.07 (5)	0.27–0.63	0.06±0.04 (3)	ND–0.13	0.04±0.01 (2)	ND–0.05	0.03±0.00 (5)	0.02–0.04	0.50±0.06 (5)	0.33–0.68
Delaware	1	1.13±0.00 (1)	—	0.07±0.00 (1)	—	0.05±0.00 (1)	—	0.07±0.00 (1)	—	0.37±0.00 (1)	—
Maryland	3	0.18±0.02 (3)	0.15–0.21	0.05±0.04 (2)	ND–0.09	0.03±0.02 (2)	ND–0.05	0.02±0.00 (3)	—	0.22±0.06 (3)	0.12–0.34
Virginia	3	0.36±0.10 (3)	0.16–0.50	0.04±0.02 (2)	ND–0.06	0.02±0.00 (1)	ND–0.02	0.03±0.00 (2)	ND–0.03	0.46±0.13 (3)	0.21–0.65
North Carolina	1	0.32±0.00 (1)	—	0.04±0.00 (1)	—	0.04±0.00 (1)	—	0.03±0.00 (1)	—	0.31±0.00 (1)	—
MALLARDS, ATLANTIC FLYWAY											
New York	3	0.53±0.19 (3)	0.25–0.89	0.08±0.05 (2)	ND–0.13	0.02±0.01 (2)	ND–0.03	0.03±0.00 (2)	ND–0.03	0.23±0.05 (3)	0.15–0.32
Pennsylvania	3	0.42±0.07 (3)	0.34–0.55	0.08±0.01 (3)	0.06–0.11	0.02±0.00 (2)	ND–0.02	0.03±0.01 (3)	0.02–0.04	1.01±0.21 (3)	0.62–1.33
New Jersey	3	0.59±0.06 (3)	0.48–0.66	0.05±0.01 (3)	0.03–0.07	0.01±0.00 (3)	—	0.02±0.00 (3)	0.02–0.03	0.52±0.09 (3)	0.39–0.70
Maryland	2	0.13±0.00 (2)	—	ND	—	ND	—	0.03±0.00 (2)	0.02–0.03	0.14±0.02 (2)	0.12–0.16
Virginia	3	0.17±0.02 (3)	0.13–0.19	0.05±0.01 (2)	ND–0.06	0.04±0.00 (1)	ND–0.04	0.23±0.00 (1)	ND–0.23	0.22±0.07 (3)	0.08–0.33
South Carolina	3[2]	0.18±0.04 (3)	0.11–0.23	0.08±0.00 (1)	ND–0.08	0.04±0.00 (1)	ND–0.04	0.01±0.00 (3)	0.01–0.02	0.16±0.02 (3)	0.13–0.19
Georgia and Florida	3	0.22±0.02 (3)	0.20–0.25	0.05±0.00 (1)	ND–0.05	0.01±0.00 (1)	ND–0.01	0.04±0.03 (3)	0.01–0.09	1.35±0.71 (3)	0.51–2.75

(*continued next page*)

TABLE 1 (cont'd.). *Organochlorine residues in pools of wings of adult mallards and black ducks, 1976–77*

State	No. of Pools	Residues, ppm Wet Weight									
		DDE		DDT		TDE		Dieldrin		PCBs [1]	
		$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range
MALLARDS, MISSISSIPPI FLYWAY											
Minnesota	5	0.18±0.03 (5)	0.11–0.25	0.07±0.01 (4)	ND–0.09	0.02±0.00 (1)	ND–0.02	ND	—	0.13±0.02 (3)	ND–0.17
Wisconsin	5	0.17±0.03 (5)	0.11–0.26	0.05±0.01 (4)	ND–0.08	0.02±0.00 (1)	ND–0.02	0.02±0.00 (4)	ND–0.02	0.22±0.02 (4)	ND–0.27
Michigan	5	0.28±0.04 (5)	0.17–0.39	0.05±0.01 (4)	ND–0.07	0.01±0.00 (1)	ND–0.01	0.04±0.01 (5)	0.01–0.09	0.37±0.11 (5)	0.14–0.81
Iowa	5	0.19±0.04 (5)	0.11–0.32	0.05±0.01 (5)	0.02–0.08	0.05±0.02 (3)	ND–0.09	0.03±0.00 (3)	ND–0.03	0.46±0.34 (2)	ND–0.80
Illinois	6	0.16±0.04 (6)	0.07–0.34	0.05±0.01 (4)	ND–0.07	0.02±0.00 (1)	ND–0.02	0.02±0.01 (4)	ND–0.03	0.14±0.01 (4)	ND–0.17
Indiana	4	0.15±0.03 (4)	0.09–0.24	0.03±0.01 (3)	ND–0.05	0.02±0.00 (1)	ND–0.02	0.02±0.01 (4)	0.01–0.04	0.13±0.03 (4)	0.10–0.21
Ohio	4	0.22±0.03 (4)	0.15–0.29	0.06±0.01 (4)	0.05–0.08	0.02±0.01 (3)	ND–0.03	0.03±0.00 (4)	0.02–0.03	0.30±0.06 (4)	0.18–0.46
Missouri	5	0.12±0.03 (5)	0.07–0.23	0.06±0.01 (5)	0.04–0.10	0.03±0.01 (2)	ND–0.04	0.01±0.00 (3)	ND–0.02	ND	—
Kentucky	3	0.29±0.11 (3)	0.15–0.51	0.06±0.02 (3)	0.03–0.08	0.02±0.00 (1)	ND–0.02	0.03±0.01 (3)	0.02–0.04	0.17±0.02 (2)	ND–0.19
Arkansas	6	0.25±0.05 (6)	0.14–0.40	0.05±0.01 (6)	0.02–0.07	0.03±0.00 (1)	ND–0.03	0.12±0.08 (5)	ND–0.45	0.12±0.00 (1)	ND–0.12
Tennessee	4	0.20±0.07 (4)	0.03–0.36	0.05±0.01 (3)	ND–0.07	0.01±0.00 (1)	ND–0.01	0.02±0.00 (3)	ND–0.03	0.21±0.06 (3)	ND–0.32
Louisiana	5	0.18±0.02 (5)	0.11–0.22	0.07±0.01 (4)	ND–0.09	0.04±0.00 (2)	ND–0.04	0.18±0.15 (5)	0.02–0.77	0.15±0.00 (1)	ND–0.15
Mississippi	6	0.46±0.08 (6)	0.18–0.66	0.15±0.03 (6)	0.05–0.28	0.02±0.00 (3)	ND–0.03	0.06±0.01 (6)	0.03–0.11	0.21±0.08 (3)	ND–0.36
Alabama	6	0.69±0.34 (6)	0.17–2.39	0.19±0.06 (5)	ND–0.41	0.38±0.33 (5)	ND–1.72	0.07±0.02 (5)	ND–0.13	0.36±0.08 (6)	0.11–0.60
MALLARDS, CENTRAL FLYWAY											
Montana (eastern)	4	0.08±0.02 (4)	0.05–0.13	0.04±0.01 (4)	0.02–0.07	0.03±0.01 (2)	ND–0.04	0.04±0.02 (3)	ND–0.06	ND	—
North Dakota	6	0.17±0.03 (6)	0.09–0.28	0.04–0.01 (5)	ND–0.06	0.02±0.00 (3)	ND–0.03	0.09±0.07 (3)	ND–0.23	ND	—
South Dakota	4	0.15±0.03 (4)	0.08–0.20	0.07±0.01 (3)	ND–0.08	0.07±0.03 (2)	ND–0.10	0.03±0.00 (1)	ND–0.03	0.14±0.00 (1)	ND–0.14
Wyoming (eastern)	4	0.07±0.01 (4)	0.05–0.08	0.06±0.01 (2)	ND–0.07	0.05±0.00 (1)	ND–0.05	0.02±0.00 (3)	ND–0.02	0.12±0.00 (1)	ND–0.12
Nebraska	8	0.07±0.01 (8)	0.03–0.16	0.05±0.01 (4)	ND–0.06	0.02±0.01 (4)	ND–0.04	0.01±0.00 (5)	ND–0.02	0.18±0.00 (1)	ND–0.18
Colorado (eastern)	6	0.12±0.02 (6)	0.07–0.19	0.06±0.01 (5)	ND–0.11	0.02±0.00 (4)	ND–0.02	0.01±0.00 (3)	ND–0.02	0.16±0.04 (2)	ND–0.20
Kansas	6	0.07±0.01 (6)	0.02–0.11	0.03±0.01 (5)	ND–0.05	0.03±0.00 (1)	ND–0.03	0.02±0.00 (2)	ND–0.02	ND	—
New Mexico (eastern)	3	1.81±0.72 (3)	0.42–2.82	0.08±0.02 (3)	0.05–0.10	0.08±0.02 (2)	ND–0.10	0.01±0.00 (2)	ND–0.01	ND	—
Oklahoma	6	0.13±0.02 (6)	0.07–0.20	0.04±0.01 (6)	0.01–0.09	0.02±0.01 (4)	ND–0.04	0.03±0.01 (6)	0.01–0.07	ND	—
Texas	9	0.17±0.01 (9)	0.09–0.24	0.04±0.01 (7)	ND–0.07	0.02±0.00 (2)	ND–0.02	0.03±0.00 (8)	ND–0.04	0.13±0.03 (2)	ND–0.16
MALLARDS, PACIFIC FLYWAY											
Washington State	8	0.20±0.02 (8)	0.14–0.27	0.07±0.01 (6)	ND–0.10	0.05±0.02 (3)	ND–0.08	0.02±0.00 (7)	ND–0.04	0.11±0.00 (1)	ND–0.11
Oregon	6	0.25±0.06 (6)	0.13–0.52	0.70±0.02 (6)	0.03–0.14	0.04±0.02 (2)	ND–0.06	0.02±0.00 (4)	ND–0.03	ND	—
Idaho	9	0.24±0.04 (9)	0.12–0.51	0.04±0.01 (9)	0.01–0.07	0.03±0.01 (6)	ND–0.06	0.02±0.00 (6)	ND–0.03	ND	—
Montana (western)	5	0.08±0.01 (5)	0.05–0.12	0.05±0.02 (4)	ND–0.09	0.02±0.01 (4)	ND–0.03	ND	—	ND	—
Wyoming (western)	2	0.08±0.01 (2)	0.06–0.09	0.08±0.02 (2)	0.05–0.10	ND	—	0.02±0.00 (2)	0.01–0.02	ND	—
California	10	0.44±0.12 (10)	0.15–1.18	0.06±0.01 (9)	ND–0.11	0.02±0.00 (7)	ND–0.04	0.05±0.01 (7)	ND–0.09	ND	—
Nevada	2	0.14±0.04 (2)	0.10–0.18	0.07±0.01 (2)	0.06–0.08	0.05±0.00 (1)	ND–0.05	ND	—	ND	—
Utah	2	0.33±0.03 (2)	0.30–0.36	0.04±0.03 (2)	0.01–0.07	0.01±0.00 (2)	—	0.02±0.00 (2)	—	0.27±0.13 (2)	0.13–0.40
Colorado (western)	3	0.13±0.02 (3)	0.10–0.15	0.09±0.02 (3)	0.06–0.12	0.04±0.01 (2)	ND–0.05	0.01±0.00 (1)	ND–0.01	0.12±0.02 (2)	ND–0.14
Arizona and New Mexico (western)	3	0.33±0.14 (3)	0.11–0.59	0.06±0.02 (3)	0.04–0.10	0.02±0.01 (2)	ND–0.03	0.02±0.00 (2)	ND–0.02	0.15±0.04 (2)	ND–0.19

NOTE: Pools contained 25 wings each. ND = not detected; — = not applicable. Values in parentheses are actual number of pools containing residues; means were calculated using these values.

[1] PCBs were quantified on the basis of Aroclor 1254.

[2] One or more pools in this group contained fewer than 25 wings.

Residues in 5 percent of the samples were confirmed by mass spectrometry. Recoveries from spiked samples ranged from 75 to 134 percent; analytical results were not corrected.

All residues are expressed as ppm wet weight. They may be converted to dry or lipid weight by dividing a given wet weight value by 0.62 or 0.13, the mean proportions of dry or lipid material, respectively, in the samples. The quantification limit was 0.01 ppm for organochlorine pesticides and PCBs. Trace residues were not reported.

Results and Discussion

Residues of DDE, DDT, TDE, dieldrin, and PCBs in duck wings for 1976 are shown in Table 1; data are arranged by state within major flyways. Because waterfowl are highly mobile species and may cover a wide range of habitats in many states, findings should not be interpreted strictly on a statewide basis. However, samples from some localities consistently contain higher residues of certain chemicals than do those from other localities (*4*), suggesting that samples are reflecting local environmental contamination. Residue levels do not indicate year-round averages because collections were made only during fall and winter.

DDE residues occurred in all wing pools, ranging from 0.02 to 2.82 ppm (Table 2); the lowest was in a pool from Kansas and the highest level was in a pool from eastern New Mexico (Table 1). PCBs were detected in all pools from the Atlantic Flyway (Table 2), ranging up to 2.75 ppm in a mallard pool from Georgia and Florida; the percentage of PCBs in samples from each flyway diminished westward. Dieldrin occurred in 62–85 percent of the samples from each flyway (Table 2), but levels seldom exceeded 0.05 ppm in individual pools. The highest level of dieldrin, 0.77 ppm, was detected in a wing pool from Louisiana.

In addition to the organochlorine compounds listed in Table 1, heptachlor epoxide, mirex, endrin, hexachlorobenzene (HCB), and chlordane isomers were found in duck wings less frequently. Since residues seldom exceeded 0.1 ppm, these chemicals were omitted from Table 1, but the percentage occurrence and ranges are listed in Table 2 by flyway.

Means of DDE, DDT, TDE, and dieldrin for the 1972 and 1976 collections, by flyway, were statistically compared to detect residue trends over time (Table 3). DDE levels remained unchanged during the 4-year period in all areas except the Pacific Flyway, where residues declined ($P < 0.01$) 36 percent. DDT levels declined ($P < 0.05$) 62 percent in the Mississippi Flyway but remained unchanged in the other flyways. Dieldrin levels did not change significantly ($P > 0.05$) in any flyway and mean residues remained quite low. Different quantification methods were used for PCBs between years; therefore, results were not compared statistically because of possible bias in the analysis.

Conclusions

Residues of DDE and DDT in mallards and black ducks have declined since 1972 in certain flyways. Geographical differences in contamination levels were detected.

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TABLE 2. *Percent occurrence and range of organochlorine residues detected in duck wings by flyway, 1976–77*

Species	Residues, ppm Wet Weight									
	DDE	DDT	TDE	Dieldrin	PCBs	Heptachlor Epoxide	Mirex	Endrin	HCB	Chlordane Isomers
ATLANTIC FLYWAY										
Black duck	100[1]	69	66	84	100	34	19	3	16	59
	0.04–1.13	0.01–0.14	0.01–0.05	0.01–0.22	0.12–1.48	0.01–0.04	0.02–0.04	0.01	0.01	0.01–0.05
Mallard	100	60	50	85	100	50	50	5	10	55
	0.11–0.89	0.02–0.13	0.01–0.04	0.01–0.23	0.08–2.75	0.02–0.17	0.01–0.14	0.02	0.01–0.03	0.01–0.06
MISSISSIPPI FLYWAY										
Mallard	100	87	38	78	61	45	29	4	7	22
	0.03–2.39	0.01–0.41	0.01–1.72	0.01–0.77	0.10–0.81	0.01–0.11	0.01–0.03	0.02	0.01–0.12	0.01–0.02
CENTRAL FLYWAY										
Mallard	100	79	45	64	13	48	14	2	9	14
	0.02–2.82	0.01–0.11	0.01–0.10	0.01–0.23	0.10–0.20	0.01–0.30	0.01–0.06	0.02	0.01–0.03	0.01–0.02
PACIFIC FLYWAY										
Mallard	100	92	58	62	14	32	4	0	24	14
	0.05–1.18	0.01–0.14	0.01–0.08	0.01–0.09	0.10–0.40	0.01–0.09	0.02–0.03	—	0.01–0.50	0.01–0.02

[1]Percent occurrence. Total number of pools per flyway: Atlantic (black ducks), 32; Atlantic (mallards), 20; Mississippi, 69; Central, 56; Pacific, 50.

TABLE 3. *Means and standard errors of organochlorine residues in waterfowl wing pools by major flyway, 1972 and 1976*

Species	Flyway	Year	No. of Pools	Residues, ppm Wet Weight				
				DDE	DDT	TDE	Dieldrin	PCBs
Black duck	Atlantic	1972	44	0.35±0.04 (44)	0.07±0.01 (44)	0.02±0.00 (44)	0.02±0.00 (44)	1.36±0.15 (44)
		1976	32	0.39±0.07 (32)	0.06±0.01 (22)	0.03±0.00 (21)	0.04±0.01 (27)	0.52±0.08 (32)
Mallard	Atlantic	1972	21	0.44±0.07 (21)	0.08±0.01 (21)	0.06±0.05 (21)	0.02±0.00 (21)	1.24±0.23 (21)
		1976	20	0.32±0.07 (20)	0.07±0.01 (12)	0.02±0.01 (10)	0.06±0.03 (17)	0.52±0.18 (20)
Mallard	Mississippi	1972	61	0.37±0.07 (61)	0.18±0.06 (61)	0.06±0.00 (61)	0.02±0.00 (61)	0.66±0.30 (61)
		1976	69	0.25±0.04 (69)	0.07±0.01[1] (60)	0.05±0.03 (26)	0.05±0.01 (54)	0.23±0.03 (42)
Mallard	Central	1972	56	0.15±0.01 (56)	0.02±0.00 (56)	0.01±0.00 (56)	0.02±0.00 (56)	0.10±0.01 (56)
		1976	56	0.28±0.17 (56)	0.05±0.01 (44)	0.04±0.01 (25)	0.03±0.01 (36)	0.15±0.01 (7)
Mallard	Pacific	1972	55	0.34±0.04 (55)	0.03±0.00 (55)	0.01±0.00 (55)	0.01±0.00 (55)	0.11±0.01 (55)
		1976	50	0.22±0.04[2] (50)	0.06±0.01 (46)	0.03±0.00 (29)	0.02±0.00 (31)	0.16±0.04 (7)

NOTE: Values in parentheses are actual number of pools containing residues; means were calculated using these values.
[1] Flyway means for the 2 years were significantly different: $P < 0.05$, analysis of variance.
[2] Flyway means for the 2 years were significantly different: $P < 0.01$, analysis of variance.

Fish and Wildlife Service. Christine Mitchell compiled the tables and performed many of the statistical computations.

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SOILS

Pesticide Residue Concentrations in Soils of Five United States Cities, 1971 —Urban Soils Monitoring Program

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ABSTRACT

Soil samples from five metropolitan areas including Baltimore, Maryland; Gadsden, Alabama; Hartford, Connecticut; Macon, Georgia; and Newport News, Virginia were analyzed for elemental arsenic, organochlorine pesticides, and polychlorinated biphenyls (PCBs). A representative number of samples were analyzed for organophosphorus pesticides, but none was detected. All areas exhibited heavy soil concentrations of organochlorine pesticides including ΣDDT, aldrin, dieldrin, photodieldrin, chlordane, heptachlor, heptachlor epoxide, endrin, endrin ketone, and endosulfan sulfate. PCBs were detected in three of the five metropolitan areas. Within the metropolitan areas, samples from the urban, or core city, locations generally had higher pesticide concentrations than did samples from suburban locations. Finally, pesticide residue concentrations were generally higher in soils of metropolitan areas than in nearby agricultural soils.

Introduction

The concept of pest control as the decrease or elimination of unwanted or menacing organisms has probably existed since the dawn of civilization. Only within the past 30 years, however, has technology advanced sufficiently to provide the degree of control now possible with chemical pesticides. Although large-scale use of pesticides is often considered an agricultural phenomenon, surveys indicate that significant amounts of the compounds are being applied in urban areas (*6*). A survey of 196 urban households in Charleston, South Carolina, showed that 89 percent used pesticides (*4*).

The published data on urban soil residues reveal that there are significant pesticide loads, comprised primarily of ΣDDT, present in United States cities. In 1963, Fahey et al. found that 89 percent of turf grass and soil samples taken in Battle Creek, Michigan, contained organochlorine pesticide residues (*2*). In that study, DDT concentrations in soil ranged from 0.07 to 79.98 ppm. Wiersma et al. confirmed the presence of pesticide loads in urban soils and noted significant variations among individual cities (*7*). In addition, overall examination of the distribution of ΣDDT within the eight urban areas sampled showed that compound concentrations were significantly higher in lawn or garden areas than in unkept or waste areas. Carey et al. found that ΣDDT concentration differed significantly between lawn and waste areas in seven of thirteen cities examined (*1*).

The present study was initiated to confirm and extend previous data by examining pesticide residues in Baltimore, Maryland; Gadsden, Alabama; Hartford, Connecticut; Macon, Georgia; and Newport News, Virginia.

Sampling Procedures

Five Standard Metropolitan Statistical Areas (SMSAs), as defined by the United States Bureau of the Census (*5*), were randomly selected from a list of all SMSAs stratified by population. Group 1 contained SMSAs with populations greater than one million, group 2 SMSAs had populations between one million and 100,000, and group 3 SMSAs had populations of less than 100,000. One metropolitan area was randomly selected from group 1, three were selected from group 2, and one was selected from group 3.

A Standard Metropolitan Statistical Area generally includes a city and all contiguous counties. In each SMSA, sampling sites were randomly allocated within the political boundaries of the city to yield a density of one site per 2.59 km^2 or one square mile. These were designated

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as urban sites. Within the adjacent counties, sites were allocated at a density of one site per 51.8 km² or 20 square miles. These were designated as suburban sites.

All sampling sites were 231 m², usually a 15.2 m by 15.2 m plot (50 ft by 50 ft). Sixteen soil cores, each 5.1 cm in diameter by 7.6 cm deep, were taken over the site on an evenly spaced, 4 by 4 grid. The cores were composited, sieved three times through a 6.3-mm mesh screen, and thoroughly mixed. A 2-liter subsample was drawn, packed in a metal container, and shipped to the Pesticides Monitoring Laboratory, Bay St. Louis, Mississippi, for analysis.

In addition, each site was designated either lawn or waste according to the criteria used by Wiersma et al. (*7*), which indicate whether the site is likely to be cultivated and/or trimmed.

Analytical Procedures

PREPARATION OF SOIL SAMPLES

A 300-g subsample of soil was taken from the sample container, moistened with 80 ml water, and extracted with 600 ml 3:1 hexane-isopropanol by concentric rotation for 4 hours. The isopropanol was removed by three distilled water washes, and the hexane extract was dried with anhydrous sodium sulfate. The sample extract was stored at low temperature for subsequent gas-liquid chromatographic analysis.

GAS-LIQUID CHROMATOGRAPHY

Analyses were performed on gas chromatographs equipped with tritium foil electron-affinity detectors for determining organohalogen compounds and equipped with thermionic or flame photometric detectors for organophosphorus compounds. A multiple-column system with polar and nonpolar columns was used to identify compounds. Instrument parameters and operating conditions follow:

Gas chromatographs:	Hewlett-Packard Model 402A Hewlett-Packard Model 402B Tracor Model MT–220	
Columns:	glass, 183 cm long × 6 mm OD, 4 mm ID, packed with 100–200-mesh Gas-Chrom Q coated with 9 percent QF-1 100–120 mesh Gas-Chrom Q coated with 3 percent DC-200 100–120-mesh Supelcoport coated with a mixture of 1.5 percent OV-17 and 1.95 percent QF-1	
Carrier gases:	5 percent methane-argon flowing at 80 ml/minute, prepurified nitrogen flowing at 80 ml/minute	
Temperatures, °C:	detector	200
	injection port	250
	QF-1 column	166
	DC-200 column	170–175
	mixed column	185–190

Sensitivity for organochlorines and trifluralin was 0.002–0.03 ppm except for combinations of polychlorinated biphenyls (PCBs), chlordane, toxaphene, and other chemicals which had minimum detectable levels of 0.05–0.1 ppm. Sensitivity for organophosphates was approximately 0.01–0.03 ppm. When necessary, identity of residues was confirmed by thin-layer chromatography or *p*-values.

TABLE 1. *Compounds detectable by chemical methodology of the present study, 1971—Urban Soils Monitoring Program*

ORGANOCHLORINES	
Alachlor	Endosulfan sulfate
Aldrin	Endrin
Chlordane	Heptachlor
o,p'-DDT	Heptachlor epoxide
p,p'-DDT	Isodrin
o,p'-DDE	Lindane (γ-BHC)
p,p'-DDE	Methoxychlor
o,p'-TDE	Ovex
p,p'-TDE	PCBs
Dieldrin	PCNs
Endosulfan (I)	Propachlor
Endosulfan (II)	Toxaphene
ORGANOPHOSPHATES	
DEF	Parathion, ethyl
Diazinon	Parathion, methyl
Ethion	Phorate
Malathion	Trithion
OTHER HALOGENS	
Trifluralin	

NOTE: Although trifluralin is a dinitroaniline compound, it is detected in the methodology used in the present study.

The compounds detectable by the methodology of the present study are listed in Table 1. Because trifluralin is detected by the organochlorine methodology it appears with organochlorine analyses in the tables.

ARSENIC

Arsenic was determined by atomic absorption spectrophotometry. The soil sample was extracted with 9.6*N* HCl, and arsenic was reduced to As^{+3} with stannous chloride. As^{+3} was partitioned from the acid to benzene, and then further partitioned from benzene to water for the absorption measurement. A Perkin-Elmer Model 303 spectrophotometer was used, and absorbance was measured with an arsenic cathode lamp at 1972 Å with argon as an aspirant to an air-hydrogen flame. Minimum detection limit was 0.1 ppm.

RECOVERY STUDIES

The average recovery rate for organochlorines, organophosphates, and trifluralin from soil was 90–110 percent. Recovery rate for arsenic was 70–80 percent. All residue levels in the tables are expressed as ppm dry weight and have been corrected for recovery.

Results and Discussion

Results of the chemical analyses are presented in Table 2. For each metropolitan area, the total number of sites is shown, as well as the arithmetic and estimated geometric mean concentrations for each compound, the minimum and maximum detected values, and the number and percent of sites with detectable concentrations.

TABLE 2. *Arsenic and organochlorine concentrations in soils from five United States cities, 1971 —Urban Soils Monitoring Program*

	Concentration, ppm Dry Weight																	
Location	Arsenic	Aldrin	Dieldrin	Photo-dieldrin	Chlor-dane	Hepta-chlor	Hepta-chlor Epoxide	Endrin	Endrin Ketone	Endo-sulfan Sulfate	PCBs	Toxa-phene	*o,p'*-DDE	*p,p'*-DDE	*o,p'*-DDT	*p,p'*-DDT	*p,p'*-TDE	ΣDDT
Baltimore, Md., 156 samples																		
Number of positive detections	156	4	29	ND	57	ND	5	ND	ND	1	6	ND	1	81	23	71	82	95
Percent of positive detections	100.0	2.6	18.7		36.8		3.2			0.6	3.9		0.6	52.3	14.8	45.8	52.9	61.3
Detected values																		
minimum	0.6	0.01	0.01		0.01		0.17			0.17	0.09		0.15	0.01	0.01	0.01	0.01	0.01
maximum	100.6	2.04	1.40		12.35		0.09				0.74		—	7.86	0.58	5.86	6.57	17.56
Arithmetic mean	7.1	0.02	0.02		0.21		<0.01			<0.01	0.02		<0.01	0.12	0.02	0.14	0.13	0.40
Estimated geometric mean	4.7	0.001	0.003		0.016		<0.001			[1]	0.001		[1]	0.013	0.003	0.014	0.015	0.031
Gadsden, Ala., 55 samples																		
Number of positive detections	55	ND	7	ND	4	ND	1	ND	ND	ND	1	ND	ND	39	7	30	11	39
Percent of positive detections	100.0		12.7		5.1		1.8				1.8			70.9	12.7	54.5	20.0	70.9
Detected values																		
minimum	1.7		0.01		0.04		0.04				11.94			0.01	0.02	0.01	0.01	0.01
maximum	25.1		0.04		0.46									0.83	0.20	1.39	0.44	2.86
Arithmetic mean	7.8		<0.01		0.07		<0.01				0.22			0.04	0.01	0.06	0.02	0.12
Estimated geometric mean	5.9		0.001		0.002		[1]				[1]			0.015	0.003	0.018	0.004	0.033
Hartford, Conn., 48 samples																		
Number of positive detections	19 [2]	4	5	ND	23	1	7	ND	ND	ND	ND	ND	2	38	15	37	25	40
Percent of positive detections	100.0	8.3	10.4		47.9	2.1	14.6						4.2	79.2	31.3	77.1	52.1	84.4
Detected values																		
minimum	1.3	0.03	0.08		0.02	0.13	0.01						0.01	0.01	0.01	0.01	0.01	0.01
maximum	50.8	0.64	1.45		140.69		1.95						0.11	1.59	0.37	2.01	1.35	4.29
Arithmetic mean	10.6	<0.01	0.06		4.00	<0.01	0.02						<0.01	0.17	0.04	0.20	0.13	0.56
Estimated geometric mean	6.4	0.003	0.004		0.067	[1]	0.004						0.001	0.046	0.010	0.058	0.019	0.123
Macon, Ga., 43 samples																		
Number of positive detections	43	ND	13	2	11	2	9	1	1	1	ND	11	4	41	33	42	11	42
Percent of positive detections	100.0		30.2	4.6	25.6	4.6	20.9	2.3	2.3	2.3		25.6	9.3	95.3	76.7	97.7	25.6	97.7
Detected values																		
minimum	0.5		0.01	0.12	0.07	0.01	0.01	0.17	0.06	0.06		0.23	0.02	0.01	0.01	0.02	0.01	0.02
maximum	5.4		6.02	0.53	0.91	0.01	0.14					4.95	0.12	1.01	0.34	1.74	0.07	3.54
Arithmetic mean	1.8		0.20	0.02	0.08	<0.01	<0.01	<0.01	<0.01	<0.01		0.24	<0.01	0.10	0.05	0.20	0.01	0.37
Estimated geometric mean	1.6		0.010	0.001	0.012	<0.001	0.004	[1]	[1]	[1]		0.019	0.002	0.049	0.027	0.097	0.004	0.175
Newport News, Va., 78 samples																		
Number of positive detections	72	ND	7	ND	10	2	3	ND	ND	ND	1	ND	ND	47	8	37	31	47
Percent of positive detections	92.3		9.0		12.8	2.6	3.8				1.3			60.3	10.3	47.4	39.8	60.3
Detected values																		
minimum	0.3		0.01		0.09	0.02	0.04				3.30			0.01	0.02	0.01	0.01	0.01
maximum	18.4		1.87		7.29	0.03	0.20							2.35	0.26	1.36	0.75	4.72
Arithmetic mean	2.4		0.04		0.16	<0.01	<0.01				0.04			0.11	<0.01	0.08	0.06	0.26
Estimated geometric mean	1.2		0.002		0.007	<0.001	0.001				[1]			0.021	0.003	0.018	0.013	0.068

NOTE: ND = not detected.

[1] Geometric mean estimate not calculated when less than two positive detections present.

[2] An additional 29 samples formed an unyielding slurry when HCl was added at the start of the extraction procedure, and could not be analyzed.

As shown in Table 2, pesticide residue data frequently contain many zero values, resulting from either the absence of pesticides or their presence at levels below the analytical sensitivity. Such data are seldom distributed normally, as shown by tests for skewness and/or kurtosis, but often approximate a log-normal distribution. After repeated tests for significant skewness and kurtosis, the log (X + 0.01) transformation was used to determine the logarithmic means. The antilogs of these figures minus 0.01 were taken to estimate the geometric mean in the untransformed dimension. The estimated geometric mean was calculated only for compounds with more than one positive detection.

ARSENIC

Elemental arsenic was detected in all five metropolitan areas and in 98 percent of all samples analyzed (Table 3). The six samples with no detectable arsenic concentrations were from Newport News sites classified as urban waste. The highest detected level of arsenic was 100.7 ppm, from an urban waste site in Baltimore.

Data for arsenic residues in Hartford were incomplete. Twenty-nine urban and suburban samples formed an unyielding slurry when HCl was added at the start of the extraction procedure, and the samples could not be analyzed. Therefore, only 19 sample results were used for the arsenic evaluation in Hartford.

Metropolitan areas were divided into two classes according to estimated geometric means of the arsenic values: high, greater than 4.7 ppm; and low, less than 1.6 ppm. Baltimore, Gadsden, and Hartford showed high levels; Macon and Newport News showed low levels. The cities sampled by Wiersma et al. showed a nearly identical division of above 5 ppm or below 2 ppm (*7*). Such overall differences among urban areas in levels of a naturally occurring element such as arsenic can probably be attributed to natural geological variation or general environmental contamination from industrial or combustion sources rather than to applications of arsenical pesticides. Neither Wiersma et al. (*7*) nor authors of the present study found significant differences in arsenic concentrations between lawn and waste areas. The difference in concentrations in urban and suburban loca-

TABLE 3. *Comparisons of detected concentrations of arsenic in soils of five United States cities, 1971 —Urban Soils Monitoring Program*

Location	Concentration, ppm Dry Weight					
			Urban		Suburban	
	Urban	Suburban	Lawn	Waste	Lawn	Waste
Baltimore, Md.						
Number of samples	74	82	44	30	10	72
Number of positive detections	74	82	44	30	10	72
Percent of positive detections	100	100	100	100	100	100
Detected values						
minimum	0.9	0.6	1.7	0.9	1.2	0.6
maximum	100.7	31.0	17.6	100.7	10.1	31.0
Arithmetic mean	8.9	5.5	6.4	12.6	5.8	5.5
Estimated geometric mean	5.6	4.1	5.2	6.3	4.8	4.0
Gadsden, Ala.						
Number of samples	30	25	15	15	7	18
Number of positive detections	30	25	15	15	7	18
Percent of positive detections	100	100	100	100	100	100
Detected values						
minimum	1.7	1.7	1.8	1.7	1.7	2.1
maximum	18.6	25.1	10.5	18.6	19.4	25.1
Arithmetic mean	6.7	9.1	6.3	7.2	6.6	10.1
Estimated geometric mean	5.6	6.2	5.4	5.7	4.4	8.6
Hartford, Conn.						
Number of samples	13	6	8	5	3	3
Number of positive detections	13	6	8	5	3	3
Percent of positive detections	100	100	100	100	100	100
Detected values						
minimum	1.9	1.3	5.0	1.9	1.8	1.3
maximum	50.8	8.3	50.8	14.7	4.3	8.3
Arithmetic mean	13.8	3.7	18.3	6.6	3.0	4.4
Estimated geometric mean	9.0	3.1	12.9	5.1	2.8	3.4
Macon, Ga.						
Number of samples	13	30	7	6	8	22
Number of positive detections	13	30	7	6	8	22
Percent of positive detections	100	100	100	100	100	100
Detected values						
minimum	0.7	0.5	0.7	1.3	0.5	0.5
maximum	4.8	5.4	2.8	4.8	2.4	5.4
Arithmetic mean	2.1	1.7	1.8	2.5	1.4	1.8
Estimated geometric mean	1.9	1.4	1.7	2.3	1.3	1.5
Newport News, Va.						
Number of samples	68	10	29	39	3	7
Number of positive detections	62	10	29	33	3	7
Percent of positive detections	91.2	100	100	84.6	100	100
Detected values						
minimum	0.3	0.5	0.3	0.3	1.5	0.5
maximum	18.4	4.6	17.8	18.4	2.3	4.6
Arithmetic mean	2.5	1.9	2.7	2.3	1.8	2.0
Estimated geometric mean	1.2	1.7	1.9	0.8	1.8	1.7

tions is probably due largely to industrial and vehicular contamination and may represent corresponding variations in air quality as demonstrated by Goodman and Robert (*3*).

ORGANOPHOSPHATES

A representative number of samples were analyzed for organophosphorus pesticides without positive results. Residues were either absent or present at concentrations below analytical sensitivity.

ORGANOCHLORINES

Concentrations of organochlorine pesticides were detected in 292, or 77 percent, of the 379 samples analyzed. ΣDDT was detected in 263, or 69 percent, of the samples analyzed. Organochlorine pesticides other than DDT detected in all five metropolitan areas included chlordane, heptachlor epoxide, and dieldrin. Four compounds, endrin, endrin ketone, photodieldrin, and toxaphene, were detected only in Macon. Sites in Baltimore contained the highest detected levels of aldrin (0.74 ppm) and ΣDDT (17.56 ppm); sites in Hartford had the highest levels of chlordane (140.69 ppm) and heptachlor epoxide (1.95 ppm). A site in Gadsden had the highest PCB level (11.94 ppm), and a Macon site had the highest dieldrin level (6.02 ppm).

Pesticide concentrations found in Macon included four compounds not found in the other metropolitan areas. Three of the compounds, endrin, endrin ketone, and photodieldrin, were detected in low concentrations of less than 0.10 ppm, generally in urban sites. Toxaphene, however, was detected in 11 suburban sites in concentations of 0.23–4.95 ppm. Previous nearby, or on-site, agricultural applications are probably responsible for the presence and unique distribution of toxaphene.

ΣDDT was detected most frequently in Macon in 98 percent of the samples analyzed; a Baltimore site had the highest concentration (17.56 ppm). Again, the five metropolitan areas could be separated into two classes of geometric mean concentrations: high, more than 0.12 ppm; low, less than 0.05 ppm. Hartford and Macon were high; Baltimore, Gadsden, and Newport News were low.

Table 4 presents a comparison of ΣDDT concentrations in soils in the urban/suburban and lawn/waste categories.

TABLE 4. *Comparison of detected concentrations of ΣDDT in soils of five United States cities, 1971 —Urban Soils Monitoring Program*

	Concentration, ppm Dry Weight					
			Urban		Suburban	
Location	Urban	Suburban	Lawn	Waste	Lawn	Waste
Baltimore, Md.						
Number of samples	74	81	44	30	10	71
Number of positive detections	64	31	39	25	2	29
Percent of positive detections	86.5	38.3	88.6	83.3	20.0	40.8
Detected values						
minimum	0.01	0.01	0.01	0.01	0.01	0.01
maximum	17.56	1.52	5.78	17.56	1.52	0.10
Arithmetic mean	0.81	0.02	0.47	1.32	0.15	0.01
Estimated geometric mean	0.096	0.007	0.090	0.106	0.008	0.007
Gadsden, Ala.						
Number of samples	30	25	15	15	7	18
Number of positive detections	25	14	14	11	4	10
Percent of positive detections	83.3	56.0	93.3	73.3	57.1	55.6
Detected values						
minimum	0.01	0.01	0.02	0.01	0.02	0.01
maximum	2.86	0.47	2.86	0.60	0.47	0.17
Arithmetic mean	0.19	0.05	0.28	0.09	0.10	0.03
Estimated geometric mean	0.052	0.018	0.069	0.038	0.029	0.014
Hartford, Conn.						
Number of samples	16	32	11	5	11	21
Number of positive detections	13	27	9	4	8	19
Percent of positive detections	81.3	84.4	81.8	80.0	72.7	90.5
Detected values						
minimum	0.01	0.01	0.08	0.01	0.05	0.01
maximum	4.29	3.89	4.29	0.08	3.89	2.79
Arithmetic mean	0.96	0.37	1.39	0.02	0.47	0.31
Estimated geometric mean	0.156	0.109	0.379	0.016	0.094	0.182
Macon, Ga.						
Number of samples	13	30	7	6	8	22
Number of positive detections	13	29	7	6	8	21
Percent of positive detections	100	96.7	100	100	100	95.5
Detected values						
minimum	0.02	0.04	0.04	0.02	0.10	0.04
maximum	3.54	1.54	3.54	0.33	1.27	1.54
Arithmetic mean	0.55	0.30	0.90	0.13	0.38	0.27
Estimated geometric mean	0.175	0.174	0.273	0.086	0.259	0.151
Newport News, Va.						
Number of samples	68	10	29	39	3	7
Number of positive detections	43	4	17	26	2	2
Percent of positive detections	63.2	40.0	58.6	66.7	66.7	28.6
Detected values						
minimum	0.01	0.02	0.02	0.01	0.04	0.02
maximum	4.72	2.07	4.72	1.97	2.07	0.06
Arithmetic mean	0.26	0.22	0.38	0.17	0.04	0.01
Estimated geometric mean	0.049	0.017	0.055	0.044	0.024	0.005

TABLE 5. *Comparison of geometric means of arsenic, ΣDDT, and chlordane in urban and agricultural soils of five states, 1971—Urban Soils Monitoring Program* [1]

Location	Concentration, ppm Dry Weight		
	Arsenic	ΣDDT	Chlordane
Baltimore, Md.	4.73	0.096	0.016
Cropland [2]	2.65**	0.007*	<0.001*
Gadsden, Ala.	5.88	0.052	0.002
Cropland [3]	1.86**	0.106**	<0.001 NS
Hartford, Conn.	6.42	0.156	0.067
Cropland [2]	2.84 NS	0.026**	<0.001**
Macon, Ga.	1.57	0.175	0.012
Cropland	1.12*	0.172 NS	0.003 NS
Newport News, Va.	1.22	0.049	0.008
Cropland [4]	2.08 NS	0.017 NS	<0.001 NS

NOTE: NS = Urban/cropland difference not significant.
* = Urban/cropland difference significant ($P < 0.05$).
** = Urban/cropland difference highly significant ($P < 0.01$).
[1] Cropland data from National Soils Monitoring Program, 1971, U.S. Environmental Protection Agency, unless otherwise indicated. Data based on t-tests of the transformed variate log (X + 0.01), U.S. Environmental Protection Agency.
[2] Mid-Atlantic States: Delaware, Maryland, New Jersey.
[3] New England States: Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, and Vermont.
[4] Virginia and West Virginia.

Frequencies of detection and levels of ΣDDT were generally higher in urban portions than in suburban portions of the SMSAs, and levels were higher in lawn sites than in waste sites. The results confirm the trend first identified by Wiersma et al. (*7*) and also demonstrated by Carey et al. (*1*).

Table 5 provides a comparison between urban and agricultural soil concentrations for arsenic, ΣDDT, and chlordane. A t-test based on the transformed variate log (X + 0.01) was used to compare mean residue concentrations between the two land use categories. For arsenic and ΣDDT, significant differences in the geometric means were detected in three of five cities; for chlordane, significant differences were detected in only two of five cities. Generally, urban areas had higher levels of pesticides than did nearby agricultural areas, except in southern cities where results varied. The contradictory results in southern cities are probably due to the traditionally heavy use of pesticides in agricultural areas of the South, as suggested previously by Carey et al. (*1*).

In summary, soils of the five metropolitan areas sampled in 1971 generally exhibited heavy concentrations of organochlorine pesticides. These results coincide with similar urban soil sampling efforts (*1, 7*). In the metropolitan areas, samples from the urban, or core city, locations generally had higher pesticide levels than did samples from the suburban locations. Finally, pesticide residue levels were generally higher in soils of metropolitan areas than in nearby agricultural soils.

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Monitoring Pesticides in Agricultural and Urban Soils of the United States [1]

Ann E. Carey [2]

ABSTRACT

Organochlorine pesticides were monitored annually in the major agricultural areas of the United States from 1968 to 1973. Results show that agricultural soils are widely contaminated with low levels of organochlorine residues. Residue concentrations are decreasing as applications of the compounds decrease. Annual monitoring of urban areas since 1969 has demonstrated that urban soils generally have higher pesticide residue concentrations than do agricultural soils in the same locations. High concentrations of mercury, cadmium, and lead have also been observed in urban soils.

Introduction

The use of pesticides in agricultural crop production in the United States has increased greatly in the past three decades. Presently, only a small percent of the population is engaged in farming. Yet this percentage not only feeds and clothes most of the United States population, but also exports to other nations. Increased use of pesticides, along with fertilizers, improved seed, new machinery, and intensive cultivation practices have contributed to this accomplishment.

Pesticides have been regulated in the United States since 1949 by the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), which was administered first by the U.S. Department of Agriculture and, since 1970, by the U.S. Environmental Protection Agency (EPA). This act was significantly revised and strengthened in 1972 and 1975. A recent provision requires EPA to monitor pesticides in components of the ambient environment. This new requirement gives legislative recognition to a cooperative pesticide monitoring effort by government agencies that has operated for several years.

The pesticide monitoring programs were initiated as a result of a recommendation in the 1963 Report of the President's Science Advisory Committee. The report urged that appropriate federal agencies develop a continuing network to monitor residue levels in air, water, soil, man, wildlife, and fish (*1*). In 1964, the U.S. Department of Agriculture began pesticide monitoring studies of agricultural soils and crops. In 1966, the results of the first monitoring studies were thoroughly evaluated, and a national design for monitoring agricultural soils was established (*9*). The design was tested on a pilot scale in 1967 (*10*) and was operated on a wide scale in calendar years 1968, 1969, 1971, 1972, and 1973. In 1970, the program was transferred to the newly created U.S. Environmental Protection Agency.

During 1968–1973 most major agricultural areas of the United States were monitored for pesticide residues (Fig. 1). Sampling was confined to the areas shown in Figure 1 and agricultural soil monitoring ceased after 1973 because of budget limitations.

In 1969, EPA initiated urban soil sampling which it has continued annually since that time. Results of each year's program have been published separately (*2, 3, 7, 11*). Currently 42 cities are sampled periodically in this program (Fig. 2). Approximately 5–10 of the cities are sampled annually, and cities are resampled every 6 years to determine changes in residues.

Sampling Procedures and Chemical Analyses

Agricultural soils are monitored at one 4-hectare site per 16,194 hectares of cropland. At each site, a composite soil sample and a composite crop sample, if available, are collected. Information on the kinds and amounts of pesticides applied to the site is also recorded.

Urban sites are 231 m^2. Composite soil samples are randomly collected at the rate of one site per 2.6 km^2 within the political boundaries of the city and one site per 51.8 km^2 in the surrounding suburbs.

All samples are analyzed for organochlorines and organophosphates by electron-capture gas chromatography (*4–6, 12*). For agricultural soils, additional analyses are performed for atrazine when use histories indicate recent

[1] This paper was presented at the 11th Congress of the International Society of Soil Science, Edmonton, Alberta, Canada, June 19–27, 1978.

[2] Ecological Monitoring Branch, Benefits and Field Studies Division, Office of Pesticide Programs, U.S. Environmental Protection Agency, TS–768, Washington, D.C. 20460.

FIGURE 1. *States where agricultural soil and crops were sampled for pesticides during 1968–73—National Soils Monitoring Program, U.S. Environmental Protection Agency*

FIGURE 2. *Metropolitan areas where soils are currrently sampled during the Urban Soils Monitoring Program, U.S. Environmental Protection Agency*

application. Urban samples are also analyzed for mercury, cadmium, and lead (*7*). All samples for the programs are analyzed at the Pesticides Monitoring Laboratory, Bay St. Louis, Mississippi. The chemicals monitored are listed in Table 1.

Results and Discussion

Representative results for organochlorine pesticides and mercury, cadmium, and lead are presented in Tables 2–7 for both the agricultural and urban soil monitoring programs. Most tables list the percent of positive detections, the arithmetic mean and/or the estimated geometric mean, and the extreme positive values detected. All data are presented as ppm dry weight, and all values have been corrected for percent recovery.

The estimated geometric mean is presented in many of the tables as an alternative to the arithmetic mean as a measure of central tendency of the data. Pesticide residue data frequently contain a large number of zero values, resulting from either the absence of pesticides or their presence at levels below analytical sensitivity. Such data are seldom distributed normally, but often approximate a log-normal distribution. Repeated tests for significant kurtosis and/or skewness resulted in use of the log $(X + 0.01)$ transformation to determine the logarithmic means. The antilogs of these figures minus 0.01 were taken to estimate the geometric mean in the untransformed dimension. The estimated geometric mean was calculated only for those compounds with more than one positive detection.

Table 2 presents the concentration changes of ΣDDT between 1968 and 1973 in United States agricultural soils. The 95 percent confidence intervals about the geometric mean are included to provide an estimate of the statistical significance of the means. The percent occurrence and the geometric mean level of ΣDDT in agricultural soils declined during the years shown. Widespread use of DDT had probably declined since the late 1960s as more reports documenting its effects were circulated in scientific and popular journals. Most uses of DDT in the United States ceased in 1973. Under the present pesticide law, the compound may still be used when considered necessary, but such uses are thoroughly reviewed by EPA before permission is granted. The confidence intervals for the geometric means for 1968 and 1973 do not overlap, indicating a probable significant difference. Additional *t*-tests on the log-transformed variates have shown that the means are significantly different.

Table 3 presents the concentration changes of aldrin, dieldrin, and toxaphene in agricultural soils sampled between 1968 and 1973. Aldrin gradually declined

TABLE 1. *Compounds monitored in agricultural and urban soils in the United States, National Soils Monitoring Program*

Organochlorines	
Alachlor	Endosulfan II
Aldrin	Endosulfan sulfate
BHC	Endrin
Chlordane	Endrin ketone
o,p'-DDT	Heptachlor
p,p'-DDT	Heptachlor epoxide
o,p'-DDE	Hexachlorobenzene
p,p'-DDE	Isodrin
o,p'-TDE	Lindane (γ-BHC)
p,p'-TDE	Methoxychlor
Dieldrin	PCBs
DCPA	Propachlor
Dicofol	Toxaphene
Endosulfan I	
Other Halogens	
Trifluralin	
Heavy Metals [1]	
Mercury	
Cadmium	
Lead	

[1] Monitored in urban soils only.

TABLE 2. *Change in ΣDDT concentrations in United States agricultural soils of 34 states, 1968–73 —National Soils Monitoring Program*

		Residues, ppm Dry Weight			
			95% Confidence Interval		
Year	% of Positive Detections	Estimated Geometric Mean	Lower	Upper	Maximum Detected Value
1968	28.9	0.015	0.013	0.017	78.36
1969	23.8	0.013	0.011	0.015	113.09
1971	23.7	0.013	0.011	0.015	388.16
1972	21.3	0.010	0.008	0.012	29.45
1973	21.5	0.007	0.006	0.008	26.76

TABLE 3. *Concentration changes in aldrin, dieldrin, and toxaphene in United States agricultural soils of 34 states, 1968–73—National Soils Monitoring Program*

	Residues, ppm Dry Weight					
	Aldrin		Dieldrin		Toxaphene	
Year	Geometric Mean	% Occurrence	Geometric Mean	% Occurrence	Geometric Mean	% Occurrence
1968	0.003	13.4	0.009	32.0	0.003	4.8
1969	0.003	14.2	0.010	32.3	0.001	2.0
1971	0.002	10.2	0.010	28.8	0.005	6.6
1972	0.002	9.4	0.009	28.1	0.004	5.4
1973	0.001	3.8	0.007	25.7	0.002	2.7

throughout the entire period. Dieldrin, its primary oxidation product, peaked about 1969, and then started to decline. Most agricultural uses of aldrin in the United States were cancelled in 1975. Toxaphene is still used today, but action is being considered to restrict or stop its use (*8*).

Table 4 presents a comparison of ΣDDT and chlordane concentrations in urban and agricultural soils sampled in 1973. To date, monitoring has shown that soils in urban areas are more heavily contaminated with the pesticides than are agricultural soils in the same locality. Only in the South, where DDT was used heavily in cotton cultivation, do the agricultural ΣDDT concentrations exceed urban concentrations.

Tables 5, 6, and 7, respectively, present concentrations of lead, cadmium, and mercury in soils from the urban and suburban portions of five metropolitan areas sampled in 1973. In general, concentrations observed for all three elements were much greater than the average background concentrations. The sources of such contamination are generally considered to be industrial processes and combustion of fossil fuels.

TABLE 4. *Comparison of ΣDDT and chlordane concentrations in United States urban and agricultural soils, 1973—National Soils Monitoring Program*

Sample	Residues, ppm Dry Weight			
	ΣDDT		Chlordane	
	% Occurrence	Geometric Mean	% Occurrence	Geometric Mean
Pittsfield, Mass.				
Urban	55.6	0.030	11.1	0.005
Agricultural	26.3	0.015	5.3	0.001
Washington, D.C.				
Urban	59.1	0.069	33.3	0.020
Agricultural	20.0	0.006	ND	—
Greenville, S.C.				
Urban	61.6	0.026	9.3	0.004
Agricultural	75.0	0.087	ND	—
Tacoma, Wash.				
Urban	34.7	0.015	14.7	0.009
Agricultural	30.2	0.010	ND	—

NOTE: ND = not detected.

TABLE 5. *Lead concentrations in urban and suburban soils of five United States cities, 1973*

Sample	Residues, ppm Dry Weight			
	% of Positive Detections	Estimated Geometric Mean	Range of Detected Values	
			Minimum	Maximum
Evansville, Ind.				
Urban	100.0	47.1	8.3	407.0
Suburban	100.0	16.1	6.3	733.0
Greenville, S.C.				
Urban	100.0	41.6	17.2	237.0
Suburban	100.0	15.9	5.0	172.1
Pittsfield, Mass.				
Urban	100.0	56.4	8.3	2136.4
Suburban	100.0	27.0	9.7	102.3
Tacoma, Wash.				
Urban	100.0	156.6	6.3	3141.4
Suburban	98.0	10.6	3.8	45.2
Washington, D.C.				
Urban	100.0	203.2	8.5	2310.0
Suburban	100.0	31.6	3.3	1840.0

TABLE 6. *Cadmium concentrations in urban and suburban soils of five United States cities, 1973*

Sample	Residues, ppm Dry Weight			
	% of Positive Detections	Estimated Geometric Mean	Range of Detected Values	
			Minimum	Maximum
Evansville, Ind.				
Urban	56.0	0.086	0.10	2.60
Suburban	28.0	0.017	0.11	1.41
Greenville, S.C.				
Urban	33.0	0.026	0.11	1.00
Suburban	3.0	0.001	0.22	0.22
Pittsfield, Mass.				
Urban	50.0	0.049	0.11	2.08
Suburban	40.0	0.029	0.11	0.75
Tacoma, Wash.				
Urban	87.0	0.378	0.13	18.00
Suburban	27.0	0.013	0.07	0.60
Washington, D.C.				
Urban	79.0	0.233	0.14	0.95
Suburban	25.0	0.010	0.14	0.83

TABLE 7. *Mercury concentrations in urban and suburban soils of five United States cities, 1973*

Sample	Residues, ppm Dry Weight			
	% of Positive Detections	Estimated Geometric Mean	Range of Detected Values	
			Minimum	Maximum
Evansville, Ind.				
Urban	100.0	0.156	0.04	3.55
Suburban	100.0	0.083	0.04	0.25
Greenville, S.C.				
Urban	100.0	0.121	0.06	1.19
Suburban	100.0	0.094	0.05	0.27
Pittsfield, Mass.				
Urban	100.0	0.249	0.11	2.51
Suburban	100.0	0.154	0.07	0.27
Tacoma, Wash.				
Urban	100.0	0.420	0.08	7.90
Suburban	100.0	0.172	0.10	0.59
Washington, D.C.				
Urban	100.0	0.246	0.07	7.81
Suburban	100.0	0.133	0.03	1.12

Conclusions

Monitoring of agricultural soils in the United States has shown that the soils are widely contaminated with low levels of the organochlorine pesticides. Residue concentrations are decreasing as applications of certain compounds decrease. Monitoring of urban areas has demonstrated that urban soils generally have higher pesticide residue concentrations than do agricultural soils in the same locations. High concentrations of mercury, cadmium, and lead have also been observed in urban soils.

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GENERAL

Organochlorine Residues in Fish, Water, and Sediment of American Falls Reservoir, Idaho, 1974[1]

James C. Kent [2] and Donald W. Johnson [3]

ABSTRACT

Organochlorine residues of TDE, DDE, and PCBs as high as 1.96, 2.79, and 28.74 μg/kg, respectively, have been found in sediments of American Falls Reservoir, Idaho. Residues of TDE, DDE, and dieldrin in the flesh of sport fish were as high as 52.3, 67.2, and 160.4 μg/kg, respectively. Maximum organochlorine residue levels found in sucker taken in the commercial fishery were 1.1 mg PCBs/kg, 781.7 μg TDE/kg, and 82.1 μg DDE/kg.

Introduction

American Falls Reservoir is located on the Snake River in Southeastern Idaho downstream from Idaho Falls and Pocatello, and is an important sport fishery for area residents. Water quality continues to be a problem in the reservoir. In 1970, the Idaho Department of Health reported that mercury concentrations in some reservoir fish exceeded the 0.5 mg/kg standard set by the Food and Drug Administration (FDA), U.S. Department of Health, Education and Welfare. The current FDA action level is 1.0 mg/kg. Officials recommended that sucker, bullhead, and yellow perch caught in the reservoir not be eaten (*29*). The fate of other pollutants, such as organochlorines, in American Falls Reservoir (AFR) and its fish had not been investigated.

The major source of pesticides has probably been contaminated sediment from irrigation and runoff. Adsorption to suspended particulate matter can place these compounds in a finely dispersed, available form which facilitates their transfer to benthic invertebrates and other silt-dwelling organisms and in turn to fish. Invertebrate populations could be affected, and in turn threaten fish populations which feed on the invertebrates (*12*).

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PCBs have become ubiquitous in world ecosystems in quantities similar to those of DDT (*4*). They also may enter the aquatic environment as do organochlorine pesticides. Silt, laden with organochlorine residues, may be carried by stream flow until it is deposited in slow-moving waters, such as reservoirs, where the organochlorines can accumulate. Forage fish, such as the Utah sucker, are vulnerable to the contaminated sediment.

Sucker are often found in large numbers in disturbed habitats, such as reservoirs, where an abundance of detrital food sources is available. Fry of the sucker are important to the diet of the AFR game fish. The fry can contribute to biomagnification; higher concentrations of organochlorines accumulate in the fish which consume them.

Health problems resulting from PCBs in the environment have been established. PCBs interfere with reproduction in rodents, fish, fowl, and primates, and they cause intestinal ailments, enlarged livers, gastrointestinal lesions, and abnormalities in the lymphatic system (*20*).

Measuring pesticides in water alone does not determine the safety of fish populations in a given habitat (*13*). Both water and sediment samples should be analyzed (*15*). These values can be combined with other biological information such as fish residue values to give an accurate pesticide pollution index (*14*).

Data reported here were collected from AFR before failure of the Teton Dam in 1976. The resultant flood waters carried large containers of pesticides and possibly spills of PCBs into the Snake River above the reservoir. Information gathered prior to the flood may provide important comparative values to help evaluate flood impact.

The objectives of the present research were to deter-

mine the levels of organochlorines in fish, water, and sediment of American Falls Reservoir; to compare the levels with standards established to protect the aquatic biota and public health; and to determine the distribution of the pollutants in the reservoir.

Methods and Materials

Water and sediment samples were collected from four stations (Fig. 1); fish were collected throughout the reservoir. Water samples were collected with a Van Doren water bottle from the mud-water interface and were placed in 1-gallon glass jars which were sealed with aluminum foil-lined lids. Sediment samples were collected with an Ekman dredge to a depth of 15 cm and were placed in 1-quart glass jars which were sealed with aluminum foil. Water and sediment samples were kept frozen for 3 months until analyses were performed.

Fish collected for residue analysis included Utah chub (*Gilia atraria*), yellow perch (*Perca flavescens*), black crappie (*Pomoxis nigromaculatus*), black bullhead (*Ictalurus melas*), and Utah sucker (*Catostomus ardens*), a forage fish. They were collected with otter trawl, gill nets, seine, and an electrofishing unit mounted on a 19-ft work boat. Whole fish were frozen except for large sucker, from which sections of epaxial muscle were taken just anterior to the dorsal fin. Samples were wrapped in aluminum foil and frozen.

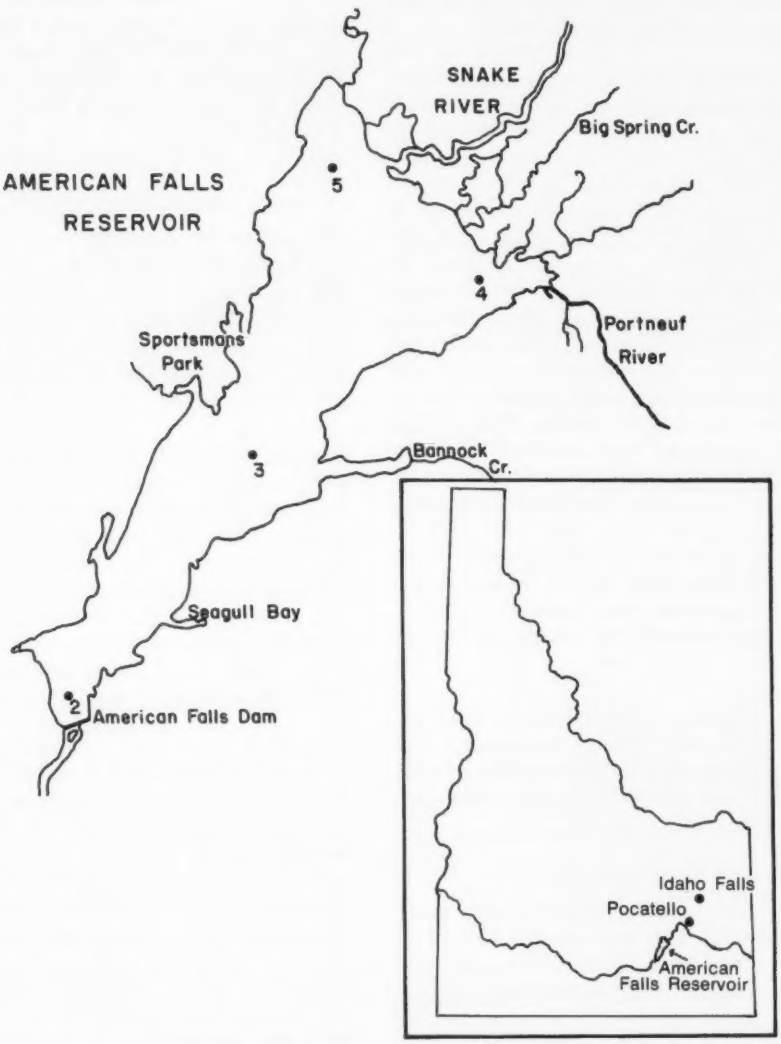

FIGURE 1. *American Falls Reservoir, Idaho, and stations sampled for organochlorine residues, 1974*

TABLE 1. *DDE, TDE, dieldrin, and PCB residues in flesh of fish over 2 years old, American Falls Reservoir, Idaho, 1974*

Species	Sample Size	Residues, µg/kg Wet Weight			
		DDE	TDE	Dieldrin	PCBs
Catostomus ardens	14	28.4±6.8[1] (1.1–82.1)	187.4±68.6 (13.9–781.7)	ND	671.7±89.0 (0–1144)
Perca flavescens	10	14.7±7.8 (2.3–28.6)	5.7±3.6 (1.2–13.4)	34.4±3.2 (0–160.4)	ND
Ictalurus melas	10	9.5±2.1 (1.0–22.6)	5.1±1.4 (0.9–14.0)	11.0±6.6 (0–48.4)	ND
Pomoxis nigromaculatus	20	20.7±4.0 (3.0–67.2)	14.0±3.1 (2.0–52.3)	ND	ND

NOTE: ND=not detected.
[1]Mean ± standard error (range).

Pesticides were separated as described by Hesselberg and Johnson (*11*). PCBs were separated from pesticides according to the method described in the *Manual of Analytical Methods* (*28*). Sulfur interference in sediment extracts was averted by adding copper.

Analyses were performed on a Hewlett-Packard, Series 7400, gas chromatograph (GC) with an electron-capture detector. Instrument parameters and operating conditions were as follows:

Column:	6-ft glass, 8 mm OD, 4 mm ID, packed with 100–120-mesh Supelcon AW-DMCS coated with a mixture of 1.5 percent SP-2250/1.95 percent SP-2401	
Temperatures, °C:	column	200
	detector	210
	injector	220
Carrier gas:	nitrogen flowing at 25 ml/minute	
Volume injected:	approximately 5 µl extract	

Each sample was analyzed for endrin, aldrin, dieldrin, hepatachlor, heptachlor epoxide, lindane, DDT, DDE, TDE, and PCBs. Compounds were quantified against an internal standard. Recovery was 85 percent, but values were not corrected for percent recovery. Quantitative and qualitative analyses of PCBs were performed by matching unknown peaks on the chromatogram to the nearest commercial preparation and by measuring the areas of four corresponding peaks with an electronic integrator (*3*). Linear regression was used in the analysis of data (*25*).

Sensitivity levels, in µg/kg, were as follows: DDT 25, DDE 5, TDE 5, endrin 50, dieldrin 2, heptachlor 2, and PCBs 2. Results were confirmed by comparison of relative retention times and by use of a dual column injected with known standards.

Results and Discussion

None of the water samples contained measurable quantities of organochlorines. This was expected because of the low solubilities of the compounds: 3.4 µg DDT/liter (*7*), 12.5 µg dieldrin/liter (*16*), and 100–1000 µg PCBs/liter (*21*).

DDE and TDE were found in all fish and sediment samples. Dieldrin was found in only two fish species, and PCBs were present in only one species. PCBs were also detected in the sediment (Tables 1, 2).

Sample areas 3, 4, and 5 had a larger mean concentration of DDE than of TDE. These areas are exposed to more turbulence, and anaerobic conditions do not develop; the reverse is true in area 2. EPA in 1973 found a similar distribution in area 2, but did not sample areas 3, 4, and 5 (personal communication). DDT and benzene hexachloride (BHC) degrade rapidly in anaerobic sediments (*6*, *19*), probably through reductive dechlorination by anaerobic bacteria (*6*). Consequently, bacteria in reservoirs are important in the degradation and removal of certain pesticides from the aquatic ecosystem. PCBs were not so ubiquitous as TDE and DDE in reservoir sediments, although two of the four areas sampled did contain a mixture of Aroclor 1248 and Aroclor 1254.

Quantities of DDT metabolites found in the present study in flesh of sucker from AFR were similar to those found in whole body samples of Ontario sucker (*5*). Dieldrin levels found in the muscle tissue of yellow perch from AFR were equal to those found in (whole body) samples of yellow perch taken from Lake Huron (*23*) and exceeded the 0.001–0.015 mg/kg levels found in yellow perch taken from lakes and streams in Ontario, Canada (*5*). Average sediment residues of DDE, TDE, and dieldrin in Ontario waters were usually much

TABLE 2. *TDE, DDE, and PCB residues in sediment of American Falls Reservoir, Idaho, 1974*

Area	Sample Size	Residues, µg/kg Wet Weight		
		TDE	DDE	PCBs
2	3	1.55[1] (1.42–1.79)	1.46 (1.18–1.73)	22.65[2]
3	3	1.04 (0.79–1.31)	2.13 (1.69–2.53)	ND
4	3	1.64 (0.53–3.60)	2.18 (1.09–3.80)	ND
5	3	1.68 (0.81–1.96)	2.21 (0.45–2.79)	28.74

NOTE: ND = not detected.
[1]Mean (range).
[2]Detected in a single sample.

higher than those found in AFR, yet sucker taken from AFR contained levels of DDE and TDE equal to or greater than those found in sucker from Ontario waters. There appears to be no correlation between sediment residue and bioconcentration in fish. Fish from McNary Refuge, Washington, contained 0.7–6.4 mg DDT and TDE/kg; 0.1–0.4 mg DDT and TDE/kg was found in associated sediments (*15*). At Deer Flat, Idaho, sediments contained 68.0–94.0 mg TDE/kg, and fish contained a maximum level of 0.2 mg TDE/kg (*15*). In a third reservoir, Tuttle Creek, Kansas, no DDT, DDE, TDE, or dieldrin was found in sediments, but all were present in fish at maximum levels of 0.17 mg DDT and dieldrin/kg (*17*). It is necessary to analyze several components of an aquatic ecosystem to establish an informative index of the pollution level.

The quantity and type of organochlorines varied considerably among species (Table 1). Dieldrin residues were detected in perch, but not in black crappie. The two species have similar diets, although mature yellow perch are more capable of bottom feeding (*22*). Consequently, perch may be more readily exposed to contaminated sediments than are black crappie. However, dieldrin was not present in sediment from the areas sampled (Table 2). Sediment analysis by the U.S. Environmental Protection Agency (EPA) in 1973 demonstrated the presence of dieldrin in one of the six areas sampled (personal communication). Presumably, exposure of fish to the contaminants depends on the areas which they inhabit and/or behavioral differences between species.

Utah sucker contained the highest concentration of organochlorines (Table 1). Constant contact of the detritus-feeding sucker with the sediment allows continuous exposure to the pesticides. This was the only species which contained PCBs, and the compound was not found in sucker less than 2 years old, possibly because the younger fish inhabit water near shore and may not be exposed to PCBs. Initial sampling indicates that PCBs are not ubiquitous in the sediments; therefore, absence of PCBs in the younger sucker may result simply from lack of exposure.

Suckers under 2 years had a greater concentration of DDE than TDE; older members of the species had a greater concentration of TDE than DDE (Table 3). This may result from metabolic changes associated with sexual maturation. Steroidogenesis may be particularly important in this metabolism (*13*). DDT metabolism has been increased by injecting rats with steroid hormones (*24*). The steroids induce the synthesis of nonspecific hepatic microsomal oxidases which increase the metabolism of DDT. The variation may also depend on the degree of exposure of the two age classes to different concentrations of DDE and TDE in the sediments. Behavioral and physiological parameters as well as availability could contribute to the residue differences observed in the fish.

Organochlorine residue levels in AFR fish were similar to residues found in fish taken from lakes and rivers used as sampling stations in the National Pesticide Monitoring Program (NPMP) conducted by EPA; however, NPMP values were calculated from whole-fish samples (*10*). American Falls Reservoir values are based on analyses of edible tissue only. The differences between values obtained for whole fish and edible tissue can be seen by comparing Tables 1 and 4. In all species except sucker and Utah chub, the concentration of pesticides in the whole fish was greater than concentrations in edible tissue. Fish used in determining whole-fish residues were younger and much smaller (1–10 g). Weights of fish analyzed for organochlorines in edible tissues were as follows: 21–2112 g, sucker; 196–600 g, black bullhead; 60–385 g, yellow perch; and 260–690 g, black crappie. Whole body residues in larger fish in the reservoir probably would be much higher than indicated by edible tissue values. The whole-fish samples analyzed indicate that residues in AFR fish exceed those reported by the NPMP. Information concerning whole-fish concentrations is most important in evaluating pesticide exposure of fish-eating birds, possible effects on the survival and maintenance of predatory game fish in the reservoir, and the exposure of animals fed rations composed of commercially caught reservoir fish. The human health threat is best evaluated by determining flesh residues which have been emphasized in the present study.

The continuance of a sport fishery in the reservoir depends on the reproductive success of all reservoir fish

TABLE 3. *DDE, TDE, and PCB residues in flesh of* Catostomus ardens *by age group, American Falls Reservoir, Idaho, 1974*

Age, Years	Sample Size	Residues, µg/kg (ppb) Wet Weight		
		DDE	TDE	PCBs
2	6	5.4±1.2 [1] (1.5–8.0)	3.0±1.1 (0–7.8)	ND
2–3	6	12.2±2.9 (1.1–19.3)	43.0±7.7 (13.9–71.4)	570±156 (0–1029)
3	8	40.5±9.8 (3.3–82.1)	295.6±106.5 (23.4–781.7)	748±104 (179–1144)

NOTE: ND = Not detected.
[1]Mean ± standard error (range).

TABLE 4. *DDE and TDE residues in whole fish samples from American Falls Reservoir, Idaho, 1974*

Species	Sample Size	Residues, µg/kg Wet Weight	
		DDE	TDE
Ictalurus melas	39	88.9[1]±11.6	127.0±26.7
Catostomus ardens	81	68.7±9.8	51.6±5.9
Pomoxis nigromaculatus	18	75.0±4.1	37.2±3.6
Perca flavescens	30	50.7±2.6	42.9±3.2
Gilia atraria	11	51.0±5.9	29.6±2.8

[1]Mean ± standard error.

populations. Several authors have studied the effects of organochlorine accumulation on the reproductive success, i.e., spermatogenesis, hatchability, time of hatching, survival, growth (*2, 8, 9, 18*). There was a direct correlation ($P < 0.05$) between the weight of the bullhead and total organochlorine residues (Fig. 2). Higher levels of organochlorine residues were found in the heavier fish. The increase in weight was associated with reproductive maturation (Fig. 2).

The Utah sucker is the predominant forage fish in the reservoir and is essential to the diet of many game spe-

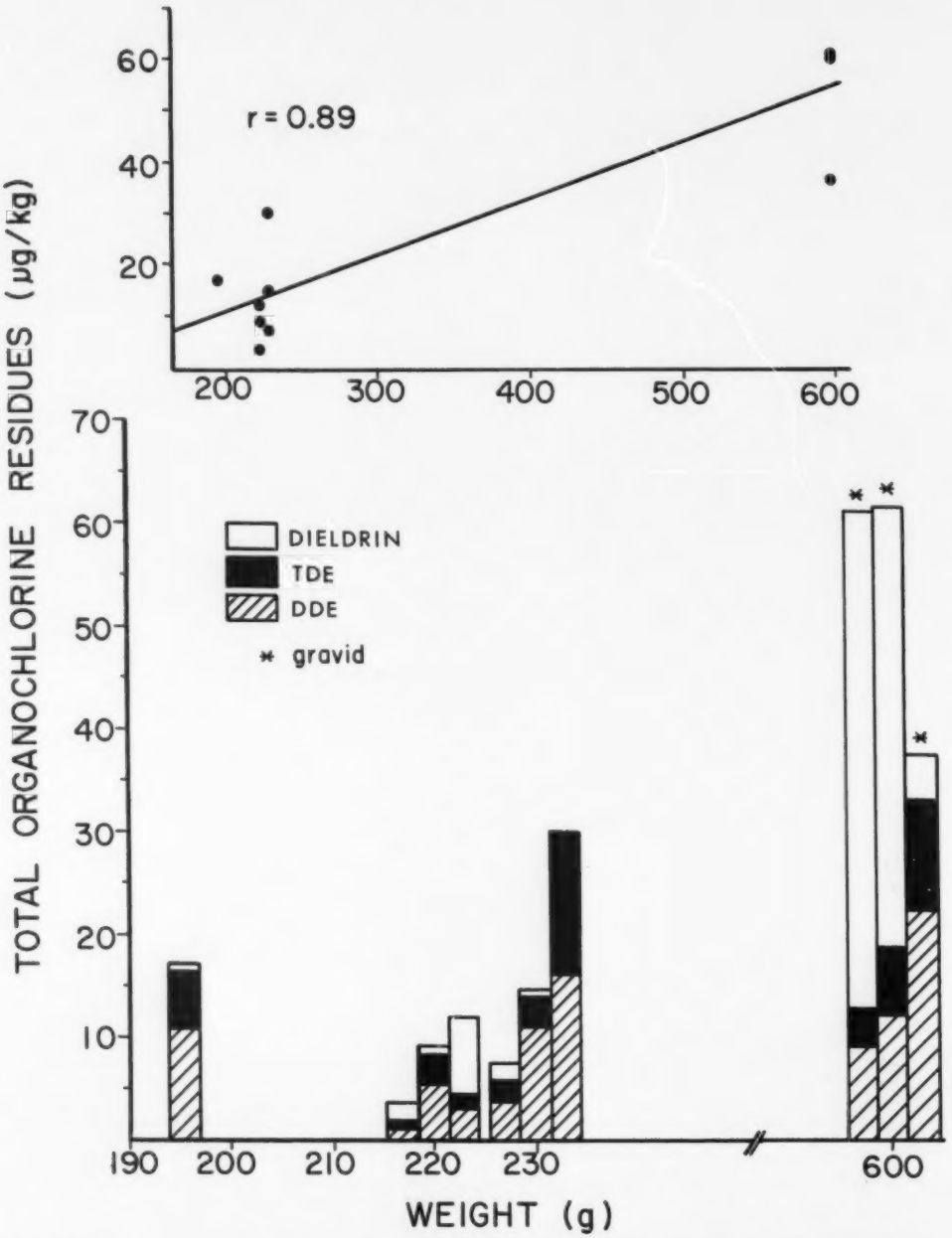

FIGURE 2. *Correlation ($P < 0.05$) between weight of the bullhead and total organochlorine residues*

cies. Reproductive success of the species is important in maintaining a stable community structure. Residues of DDT metabolites and PCBs are higher in the Utah sucker than in other reservoir species. Sucker are among the species most susceptible to organochlorines (*27*). Although no PCBs were found in AFR water, the possible effects of PCBs on reproduction remain.

During the summer of 1975, 75 percent of the sucker collected had fungus-like growths on their heads and sides. Similar symptoms developed when pinfish were exposed to 5 μg Aroclor 1254/liter (*26*). After the pinfish were returned to flowing water, free from PCBs, most died. Much higher concentrations were found in the larger sucker of American Falls Reservoir than in the experimentally exposed pinfish. Although PCBs in the reservoir were not demonstrated to have directly caused the lesions and fungus-like growths on the sucker, it is a possible explanation.

Chlorinated hydrocarbon residues in American Falls Reservoir did not exceed the FDA recommended action levels of 5 mg DDT/kg, 0.3 mg dieldrin/kg, and 5 mg PCBs/kg. In the larger sucker harvested by the commercial fishery, DDT approached 1 mg/kg. At this level, EPA previously recommended that precautionary measures should be taken to avoid endangering the health of those who consume the fish (*21*). However, the current FDA and EPA view is that this level does not present a hazard (J. R. Wessel, FDA, personal communication, 1973).

EPA has recommended that PCB concentrations in any sample consumed by any bird or mammal be no greater than 0.5 mg/kg (*21*). The Fish and Wildlife Service, U.S. Department of the Interior, regards the presence of 0.5 mg PCBs/kg in a fish as indicative of pollution (*1*). Average PCB level in sucker from American Falls Reservoir was 0.67 mg/kg; hence consumption of fish from the reservoir may harm some of their predators.

Acknowledgments

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Mercury, Arsenic, and Cadmium in Fish, Water, and Sediment of American Falls Reservoir, Idaho, 1974[1]

James C. Kent [2] and Donald W. Johnson [3]

ABSTRACT

Mercury and cadmium were found in fish, water, and sediment of American Falls Reservoir (AFR), Idaho. Mercury and cadmium levels in some fish exceeded human health standards set by the Food and Drug Administration, U.S. Department of Health, Education and Welfare, and the World Health Organization. Analyses performed on the flesh of rainbow trout showed mercury residues of up to 1.20 mg/kg, which were higher than residues previously reported in trout collected in 1970 and 1971 from AFR. Cadmium residue levels were as high as 0.80 mg/kg. Although arsenic was found in reservoir sediment at levels of 1.36–2.40 mg/kg, it was not detected in fish.

Introduction

The pollution of aquatic ecosystems by heavy metals has received greater attention since the discovery of mercury as the cause of Minamata disease in Japan in the 1950s (*39*). Recent studies of fish from Idaho, California, Oregon, and Washington state revealed levels up to 1.9 mg mercury/kg (*11*), which were above the 1.0 mg/kg action level set by the Food and Drug Administration (FDA), U.S. Department of Health, Education and Welfare. Although mercury has received the most attention, other metals, such as arsenic and cadmium, may also contribute to pollution of aquatic ecosystems.

Cadmium—Isolated incidents of cadmium pollution have been reported. In 1970, cadmium was identified as the cause of the Japanese disease itai-itai. It was contracted by eating rice that had been irrigated with river water polluted by runoff from cadmium mines (*13*). A survey of 720 lakes and rivers in the United States revealed that water from only 4 percent of the samples contained more than 10 μg cadmium/liter (*1, 36*). Phosphate fertilizers contain 50–170 mg cadmium/kg (*2*). Waters in phosphate mining and processing areas of Idaho, as well as downstream reservoirs, have been monitored for potential cadmium pollution (*18*).

Arsenic—Arsenic was found in less than 6 percent of the waters sampled in 1962 by the Federal Water Quality Administration. In waters containing colloidal materials, the dissolved arsenic content may be decreased by adsorption. Water samples from Lake Erie contained an average of 38 μg arsenic/liter (*13*). Mean values of 5.6–80.0 μg arsenic/kg were found in 15 species of fish from the Great Lakes (*12*). However, the effect of arsenic accumulation in aquatic organisms is not well documented.

Mercury—Reservoirs act as a trap for silt and suspended particulate matter in runoff. Metals concentrated in the bottom sediments may be available to detrital-feeding organisms. Biomagnification of metals may produce fish unfit for repeated consumption. This has been the case in Idaho. In 1970, the Idaho Health Department collected 160 fish from Idaho waters and analyzed them for mercury. Nineteen percent of the samples exceeded the previous FDA standard of 0.5 mg/kg (*12*). Thirty percent of the fish taken from American Falls Reservoir (AFR), Idaho, had mercury levels exceeding 0.5 mg/kg. Similar mercury concentrations were found in fish taken from other impoundments in the lower and middle Snake River. Further investigations in 1971 revealed that rainbow trout (*Salmo gairdneri*) in AFR had a mean residue level of 0.33 mg mercury/kg and a maximum of 0.91 mg/kg (*12*). Elevated mercury levels were also detected in brown trout (*Salmo trutta*) and cutthroat trout (*Salmo clarki*). Yellow perch (*Perca flavescens*) from the reservoir had a mean concentration of 0.47 mg mercury/kg in muscle tissue; values ranged from 0.09 to 0.84 mg/kg; 57 percent of the yellow perch sampled contained residues at or above 0.5 mg/kg (*12*). A follow-up study in 1972 found a mean of only 0.19 mg mercury/kg in yellow perch (*19*).

The objectives of the present study were to determine mercury, arsenic, and cadmium concentrations in fish,

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water, and sediment of AFR; to compare the concentrations of heavy metals with action levels established to protect aquatic biota and public health; and to determine the distribution of the pollutants within the fish community.

Study Area

American Falls Reservoir is located on the Snake River in southeastern Idaho downstream from Idaho Falls and Pocatello (Fig. 1). The upper Snake and Portneuf River watersheds are the major sources of reservoir waters; however, springs contribute as much as 22 percent of the reservoir inflow.

The most abundant game fish in the reservoir are yellow perch and hatchery-stocked rainbow trout. Black crappie (*Pomoxis nigromaculatus*) and black bullhead (*Ictalurus melas*) also enter the sport catch. Angling pressure at the reservoir is between 15,000 and 25,000 angler days annually (*15*). The most numerous native species include Utah sucker (*Catostomus ardens*) and chub (*Gilia atraria*). Introduced nongame species include redside shiner (*Richardsonius balteatus*) and carp (*Cyprinus carpio*). Carp and sucker are harvested commercially and sold for human consumption and as a component for fish food.

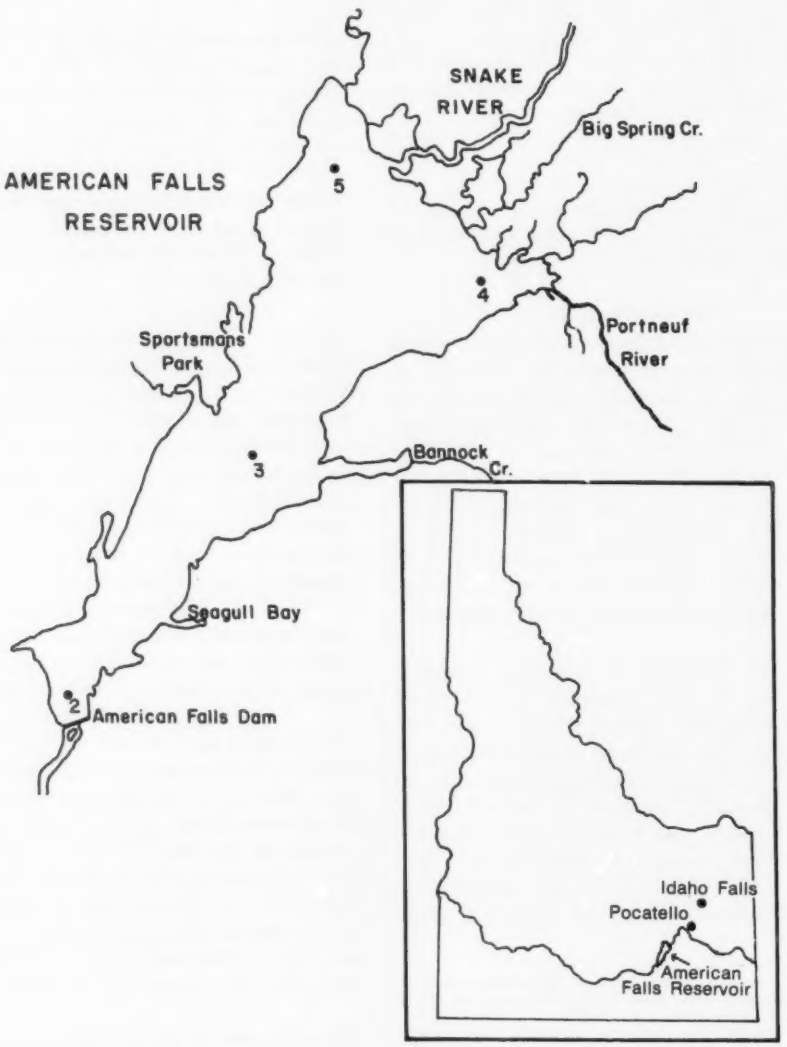

FIGURE 1. *American Falls Reservoir, Idaho, and stations sampled for heavy metal residues, 1974*

Methods of Study

Sediment and water samples were collected from four areas of the reservoir to determine the presence and distribution of cadmium, arsenic, and mercury (Fig. 1). Fish sampling was not restricted to these stations.

Water samples were collected with Van Dorn water bottles at the sediment-water interface and placed in 1-liter plastic containers to which concentrated nitric acid was added (*41*). Sediment samples were collected by Ekman dredge, to a depth of 15 cm, and placed in 1-quart glass jars which were sealed with aluminum foil.

The edible flesh of five species of fish was analyzed, including rainbow trout, yellow perch, black crappie, black bullhead, and the predominant forage fish, Utah sucker.

Analyses were performed on a Varian Model 1200 atomic absorption spectrophotometer equipped with a Model 63 carbon rod atomizer and the Model 64 As/Se/Hg Analysis Kit. A Neff Model 401 recorder was used to record results.

Mercury levels in fish, water, and sediment were determined by vapor generation (*28*). Arsenic was determined by the method of Duncan and Parker (*28*). Cadmium in water was determined by direct application of sample extracts to the carbon rod unit. Fish samples, 0.5 g, were first digested with 10 ml nitric acid (*9*). Sediment samples, 0.5 g, were digested with 10 ml nitric acid and diluted to 20 ml with distilled water. Fish and sediment samples were also analyzed directly on the carbon rod.

Spiked samples yielded 85 percent recoveries but results are reported at the conservative uncorrected values. Sensitivity for mercury, cadmium, and arsenic are, respectively, 2, 5, and 20 μg/kg.

Results and Discussion

The U.S. Environmental Protection Agency (EPA) in 1973 had determined the concentration of arsenic, mercury, and cadmium in AFR water (personal communication). Mercury accumulations in water, sediment, and trout, as well as other game fish, have also been determined (*35*). Each of the reports was based on analysis of only one component or one contaminant in the aquatic ecosystem. The present study on AFR has taken a broader approach (Tables 1–3). Cadmium and mercury were found in water, sediment, and fish. Arsenic was found only in the water and sediment. Examination of only one contaminant may fail to reveal hazards to the aquatic ecosystem. Synergistic or additive effects of multiple contaminants could render lethal so-called safe environmental levels of any single contaminant.

TABLE 1. *Mercury, cadmium, and arsenic residues in water and sediment, American Falls Reservoir, Idaho, 1974*

Location [1]	No. of Analyses	Mean Concentration (Range), Wet Weight		
		Mercury	Cadmium	Arsenic
Area 2				
Water [2]	3	0.72 (0.25–1.52)	9.23 (6.42–11.26)	12.60 (1.50–33.0)
Sediment [3]	3	350 (210–420)	620 (600–640)	2020 (1570–2400)
Area 3				
Water	3	0.70 (0.45–1.20)	14.64 (6.62–24.47)	15.67 (3.0–25.50)
Sediment	3	490 (420–530)	390 (360–640)	1830 (1380–2200)
Area 4				
Water	3	1.02 (0.55–1.78)	6.64 (1.67–10.63)	16.50 (3.50–30.50)
Sediment	3	530 (210–950)	430 (140–720)	1560 (1400–1750)
Area 5				
Water	3	1.02 (0.30–1.47)	5.95 (1.0–9.67)	4.67 (3.0–8.0)
Sediment	3	320 (320–320)	940 (640–1240)	1380 (1360–2040)

NOTE: Water values in excess of the following are considered by EPA to constitute an environmental threat: mercury, 0.2 μg/liter; cadmium, 2.0 μg/liter; arsenic, 50.0 μg/liter.

[1] See Figure 1.
[2] μg/liter.
[3] μg/kg.

TABLE 2. *Mercury residues in fish of American Falls Reservoir, Idaho, 1974*

Species	Sample Size	Residues, mg/kg (ppm), Wet Weight		
		Mean	Std Error	Range
Catostomus ardens	15	0.37	0.06	0.10–0.82
Perca flavescens	10	0.19	0.02	0.11–0.33
Ictalurus melas	10	0.17	0.03	0.10–0.34
Pomoxis nigromaculatus	14	0.37	0.06	0.12–0.80
Salmo gairdneri				
Hatchery stock (<20 cm)	16	0.13	0.02	0.05–0.30
Carry-over (>20 cm)	13	0.60	0.08	0.12–1.20

TABLE 3. *Cadmium residues in fish of American Falls Reservoir, Idaho 1974*

Species	Sample Size	Residues, mg/kg (ppm), Wet Weight		
		mean	Std Error	Range
Catostomus ardens	16	0.19	0.04	0.08–0.60
Perca flavescens	9	0.23	0.03	0.14–0.44
Ictalurus melas	10	0.15	0.05	0.04–0.30
Pomoxis nigromaculatus	16	0.19	0.03	0.03–0.45
Salmo gairdneri (>20 cm)	12	0.51	0.04	0.32–0.80

Cadmium—Cadmium concentrations of 1.0–24.5 μg/liter were found in AFR water. Most lakes and rivers in the United States contain 10 μg/liter or less. Analysis of 720 lakes and rivers revealed that 41 percent had concentrations of 1–10 μg/liter, 4 percent of the waters contained 12–130 μg/liter (*7*). Values from AFR were similar to those from Foundry Cove, Hudson River, a known recipient of cadmium waste. The concentration in Foundry Cove ranged from 5 to 26 μg/liter (*36*). The National Academy of Sciences considered 3.0 μg/liter a threat to aquatic life (*26*).

Cadmium concentrations in the Illinois River were as follows: water, 0.10–2.0 μg/liter; sediment, 0.2–12.1 mg/kg, with a mean of 2.0 mg/kg; and fish, 0.03 mg/kg (*24*). Hudson River water contained little dissolved cadmium, 3.0–6.0 μg/liter, but the mud contained 162 mg/kg. Water from three Alabama rivers had 6.1, 65, and 90 μg cadmium/liter; however, cadmium was found only at the source and not downstream. Fish from the same rivers contained a maximum of 0.8 mg/kg, compared to 0.2–304 mg/kg found in Hudson River fish (*36*). This confirms the advisability of monitoring sediment concentrations, as well as levels in water. In these cases, no correlation was found between water and sediment concentrations. This was also true for AFR; linear regression analysis of cadmium in water and sediment indicates no correlation at the 0.05 significance level. Cadmium concentration in the AFR sediments was low (Table 1).

Cadmium was not mobilized from sediments as readily as mercury, nor was it concentrated in fish to the same degree (Table 3). The high calcium carbonate content of AFR water may decrease the availability and toxicity of cadmium to fish by forming a cadmium carbonate precipitate in sediments (*30*). Exposure to cadmium may depend on ingestion of contaminated biota or particulate matter. There is no evidence that cadmium is absorbed across the gill epithelia. Zinc values for rainbow trout, Utah sucker, yellow perch, and bullhead taken from AFR have been as high as 12.8, 9.2, 11.4, and 1.05 mg/kg, respectively (*27*). Cadmium appears to accumulate in larger amounts when absorbed with zinc than when it is absorbed alone as indicated by acute toxicity tests with cadmium alone (*8*).

Cadmium concentrations of 0.06–1.4 mg/kg were found in Great Lakes fish (*23*). Black bullhead, sucker, black crappie, and yellow perch from New York waters had mean levels of 27.3, 23.1, 14.7, and 51.0 μg cadmium/kg, respectively (*22*). In the present study and in the New York investigation, no correlation was found between size of fish and level of cadmium concentration. Data indicate that the 150–510 μg/kg values for cadmium in fish from AFR are high.

Daily intake of cadmium from all food sources averages 50 μg/day in the United States (*10*). The FDA has stated that at this level "we may have reached the safe upper limit for cadmium" (*3*). Consumption of fish from AFR would increase daily intake of cadmium in excess of the World Health Organization-suggested maximum intake of 70 μg/day.

Arsenic—Arsenic compounds occur naturally in some waters of the western United States (*25*). In AFR water, arsenic concentrations ranged from 1.5 to 33 μg/liter (Table 1). Similar values have been reported in other areas of the country. Water in Kansas contained 2.6 μg arsenic/liter, although Lake Erie and the St. Lawrence River contained only 0.308 and 0.58 μg/liter, respectively (*13, 29*).

Arsenic is readily adsorbed by colloidal and suspended matter and transported to the sediment (*26*). In AFR, a significant correlation ($P < 0.05$) existed between water turbidity and arsenic concentration. Arsenic in sediment ranged from 1.36 to 2.40 mg/kg.

Accumulation in fish depends on the valence state of arsenic. Fish collected from a lake 21 days after application of arsenic showed no significant increase in arsenic accumulation, although water concentrations reached a maximum of 7.0 mg/liter (*40*). Arsenic was not found in AFR fish.

Mercury—The maximum mercury level found in AFR water was 1.78 μg/liter. The Idaho Health Department found a maximum of 1.8 μg/liter, and Runyan found 1.3 μg/liter (*35*). Mercury concentrations were found in 27 of 73 rivers in the United States at levels of 0.1–1.0 μg/liter (*42*). Groundwaters have contained 0.02–0.07 μg/liter (*5*). Mercury levels in AFR were 70–100 times higher than levels found in Lake Powell (Colorado River) (*31*), although a higher level, 2.1 μg/liter, has been measured in surface waters of Lahontan Reservoir in Nevada (*33*). These values are far higher than the 0.03 μg/liter level presumed to be the mean natural content of uncontaminated water (*6*) and the EPA no-effect criterion of 0.05 μg/liter (*26*).

Mercury exhibits a distribution between water and sediment similar to that of cadmium. Mean mercury concentrations in AFR sediment ranged from 0.32 to 0.53 mg/kg, 300–700 times the concentration found in the water (Table 1). In Lake Powell, 0.03 mg/kg was found in the sediment, but concentrations in water were only 0.01 μg/liter (*31*). Values reported after California investigations ranged from 0.04 to 33.0 mg/kg in sediments (*4*). Methylation of mercury by bacteria in the sediment significantly increases the availability of mercury for absorption across the gills of fish (*34*).

Background levels of mercury in noncontaminated fish are generally less than 0.2 mg/kg (*6*). Mean values of mercury in AFR yellow perch, black bullhead, and hatchery-stocked trout did not exceed this value. Utah sucker, black crappie, and large rainbow trout have mean values greater than 0.2 mg/kg (Table 2). These values approach the previous FDA public health standard of 0.5 mg/kg for fish flesh (*11*). Thirteen percent of the Utah sucker, 21 percent of the black crappie, and 60 percent of the large rainbow trout exceeded this standard. The mean value of mercury for all fish from AFR was 0.30 mg/kg. By contrast, fish from Lake

Powell contained 0.23 mg/kg (*31*); from Ross Barnett Reservoir, Mississippi, 0.05–0.74 mg/kg; and from Lahontan Reservoir, Nevada, 0.20–2.72 mg/kg (*20, 33*). Mercury concentrations in hatchery trout and yellow perch from AFR were similar to those found in 1971 (*35*). However, the mean concentration in black bullhead was only 0.17 mg/kg compared to 0.36 mg/kg found in 1971, and the sucker value was 0.37 mg/kg compared to 0.11 mg/kg found in 1971.

Physical attributes of fish as well as chemical and physical characteristics of aquatic systems may limit, enhance, or modify the uptake and toxicity of heavy metals to fish. Runyan reported no correlation between weight and mercury concentration in rainbow trout from AFR, but a significant correlation was found between length and mercury concentration (*35*). Jarmon found a positive correlation between mercury concentration in muscle and the age and length of yellow perch from American Falls and Western Reservoirs in Idaho (*17*). Other authors have reported no correlation between either weight or length and concentration of mercury (*37, 43*). There was no significant correlation between weight, age, length, or condition factor and mercury concentration for any species analyzed in the present study. Chronic exposure to low levels of mercury may cause fish to acquire similar tissue concentrations regardless of size (*16*). Fish of the same size and species, exposed identically, have shown maximum concentrations up to 10 times the minimum (*14*).

Methylation of mercury by bacteria in sediments is a critical step toward increasing mercury availability to fish. These processes occur more readily under aerobic than anaerobic conditions. The rate of methylation has been directly related to the presence of nutrients such as carbon, phosphate, nitrogen, and other trace elements, presumably because they stimulate the growth of methylating bacteria (*21, 38*).

The amount of soluble inorganic mercury in the water absorbed by fish is also pH dependent. Under alkaline conditions, as in AFR, inorganic mercury is released from the sediment into the water (*38*). Noncomplexed inorganic mercury is, however, not readily absorbed by fish from water with a high pH. Halides, such as fluorides, present in AFR, may form complexes with inorganic mercury and facilitate its absorption by fish. Hydrogen sulfide which develops in the anaerobic bottom waters of the reservoir may be brought to the surface waters when overturn occurs in autumn. This would facilitate exposure and absorption of inorganic mercury at all levels of the water column (*38*). Increased temperature may also increase the uptake of both organic and inorganic mercury (*1, 32*). In rainbow trout, lethal levels of mercury decreased with increased water temperature, increased chloride ion content, or decreased oxygen (*1*). It appears, therefore, that ambient water conditions at the time of exposure are more significant to exposed fish than are age, weight, length, condition factor, or contaminant concentration.

Conclusions

Modification of toxicity by chemical and physical parameters emphasizes the need to redefine safe levels in aquatic environments. Each aquatic system is unique, and safe levels of contaminants should be determined which reflect the characteristics of the system.

Elevated mercury and cadmium levels have been identified in fish, sediment, and water. The levels present exceed those at which protection of aquatic species is recommended by EPA. The source of the pollutants is unidentified as is their potential to measurably degrade the health, growth, and reproductive success of the reservoir fishery.

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALACHLOR	2-Chloro-2′,6′-diethyl-*N*-(methoxymethyl)-acetanilide
ALDRIN	Hexachlorohexahydro-*endo,exo*-dimethanonaphthalene 95% and related compounds 5%
AROCLOR 1016 or 1242	PCB, approximately 42% chlorine
AROCLOR 1248	PCB, approximately 48% chlorine
AROCLOR 1254	PCB, approximately 54% chlorine
BHC (Benzene Hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
CHLORDANE	1,2,3,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene. The technical product is a mixture of several compounds including heptachlor, chlordene, and two isomeric forms of chlordane.
CHLORDENE	4,5,6,7,8,8-Hexachloro-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene
DCPA	Dimethyl-2,3,5,6-tetrachloroterephthalate
DDE	Dichlorophenyl dicholoro-ethylene (degradation product of DDT); *p,p′*-DDE: 1,1-Dichloro-2,2-bis(*p*-chlorophenyl) ethylene; *o,p′*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethylene
DDMU	1-Chloro-2,2-bis(*p*-chlorophenyl) ethylene
DDT	Main component (*p,p′*-DDT): *α*-Bis(*p*-chlorophenyl) *β,β,β*-trichloroethane. Other isomers are possible and some are present in the commercial product. *o,p′*-DDT: 1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane
DICOFOL	1,1-Bis(chlorophenyl)-2,2,2-trichloroethanol
DIELDRIN	Not less than 85% of 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7:8,8a-octahydro-1,4-*endo*-*exo*-5,8-dimethanonaphthalene
ENDOSULFAN	Hexachlorohexahydromethano-2,4,3-benzodioxathiepin 3-oxide
ENDOSULFAN SULFATE	1,4,5,6,7,7-Hexachloro-5-norbornene-2,3-dimethanol cyclic sulfate
ENDRIN	Hexachloroepoxyoctahydro-*endo-endo*-dimethanonaphthalene
ENDRIN KETONE	1,8,9,10,11,11-Hexachloropentacyclo[6.2.1.$0^{2,7}$.$1^{3,6}$.$0^{5,9}$]dodecan-4-one
HCB	Hexachlorobenzene
HEPTACHLOR	1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-*endo*-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindene
ISODRIN	Hexachlorohexahydro-*exo,exo*-dimethanonaphthalene
LINDANE	*Gamma* isomer of 1,2,3,4,5,6-hexachlorocyclohexane
METHOXYCHLOR	2,2-Bis(*p*-methoxyphenyl)-1,1,1-trichloroethane 88% and related compounds 12%

(Continued next page)

APPENDIX (*continued*)

MIREX	1,1a,2,2,3,3a,4,5,5,5a,5b,6-Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
NONACHLOR	1,2,3,4,5,6,7,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindan
OVEX	*p*-Chlorophenyl *p*-chlorobenzenesulfonate
OXYCHLORDANE	2,3,4,5,6,6a,7,7-Octachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2*H*-indeno(1,2-β)oxirene
PCBs (Polychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
PCNs (Polychlorinated Naphthalenes)	Mixtures of chlorinated naphthalenes
PHOTODIELDRIN	3,4,5,6,7-Hexachloro-12-oxahexacyclo[6.5.0.0^{2,10}.0^{3,7}.0^{5,9}.0^{11,13}]tridecane
PHOTOMIREX	1,2,3,4,5,5,6,7,9,10,10-Undecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane
PROPACHLOR	2-Chloro-*N*-isopropylacetanilide
TDE	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products)
TOXAPHENE	Chlorinated camphene (67–69% chlorine). Product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating.
TRIFLURALIN	α,α,α-Trifluoro-2,6-dinitro-*N*,*N*-dipropyl *p*-toluidine

The *Pesticides Monitoring Journal* welcomes from all sources qualified data and interpretative information on pesticide monitoring. The publication is distributed principally to scientists, technicians, and administrators associated with pesticide monitoring, research, and other programs concerned with pesticides in the environment. Other subscribers work in agriculture, chemical manufacturing, food processing, medicine, public health, and conservation.

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